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PART II

HYBRID FLUOROSILICONES FOR AIRCRAFT FUEL TANK SEALANTS

SYNTHESIS OF FLUOROCARBON AND FLUOROCARBON ETHER HYBRID FLUOROSILICONE POLYMERS

Ogden R. Pierce
Yung K. Kim
George A. Grindahl

DOW CORNING CORPORATION

TECHNICAL REPORT AFML-TR-70-278, PART II

February 1972

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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HYBRID FLUOROSILICONES FOR AIRCRAFT FUEL TANK SEALANTS

Synthesis of Fluorocarbon and Fluorocarbon Ether Hybrid Fluorosilicone Polymers

Ogden R. Pierce
Yung K. Kim
George A. Grindahl

FOREWORD

This report was prepared by the Advanced Research Department, Dow Corning Corporation, Midland, Michigan 48640, under Contract No. F33615-71-C-1311, Project No. 7340 "Nonmetallic and Composite Materials", Task No. 734005 "Elastomeric and Compliant Materials". It was administered under the direction of the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433, with Mr. W. R. Griffin (LNE) acting as Project Engineer. This report was submitted January, 1972.

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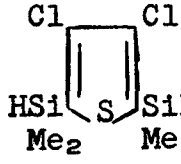
ABSTRACT

The objective of this exploratory development is the synthesis and evaluation of hybrid fluorosilicone sealants for possible use as integral fuel tank sealants and other applications in high performance aircraft.

The synthesis of alpha,omega-difunctional fluorocarbon ethers was accomplished from both $BrCF_2CF_2COF$ and $FOC(CF_2)_3COF$ in which the functional groups were either bromine or iodine. An additional starting material, $FOCCF_2OCF_2COF$ was successfully prepared starting with 1,4-hexachlorobutadiene. It was found that these functional fluorocarbon ethers could be coupled to form short polymer chains using mercury. Initial studies of the coupling of alpha,omega-diiodofluorocarbons with aromatic halides were successful indicating that such compounds can be prepared in good yield.

The polymerization of the monomer,  , furnished by AFML gave a stiff gum which was given preliminary evaluation. The polymer was only moderately stable but did show some fire retardant properties. A second monomer, $HSi(CH_3)_2(CF_2)_6(CH_3)_2SiH$, gave extensive decomposition when polymerization was attempted.

A hybrid fluorosilicone-fluoroether (FES) sealant was prepared containing the ether unit, $-CF_2CF_2O(CF_2)_{2,3}-$ in the polymer backbone. It is presently being evaluated in our laboratories.

A sample of formulated sealant (in excess of one pound) prepared as a random copolymer of FCS-610 and poly(3,3,3-trifluoropropyl)methylsiloxane was submitted to AFML (LNE) for evaluation.

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SECTION

I. Introduction

The objective of this exploratory development program is to synthesize and evaluate hybrid fluorosilicone sealants for possible use in integral fuel tanks and other areas of high performance aircraft. Of particular interest are the improvements possible in fuel and reversion resistance, thermal and oxidative stability and low temperature flexibility.

Previous work conducted in this laboratory and described in AFML-TR-70-278, Part I has demonstrated that a hybrid fluorosilicone polymer of the unit structure,

$$[O\text{-}\underset{R'}{\overset{R}{Si}}CH_2CH_2ZCH_2CH_2\underset{R'}{\overset{R}{Si}}\text{-}]_x,\ R = CH_3,\ R' = CF_3CH_2CH_2,\ Z =$$

$(CF_2CF_2)_n$ or $-CF(CF_3)O(CF_2)_5O(CF_3)CF-$ (mixed isomers) possessed many desirable properties but was lacking in oxidative stability and low temperature flexibility. Consequently, during the past year effort was directed toward modification of this structure to overcome these difficulties. In one approach, additional siloxane units were incorporated in the polymer backbone to achieve increased low temperature flexibility as measured by Tg. Another direction encompassed the study of the preparation of aliphatic fluorocarbon ethers with functional end groups. A third effort was devoted to the replacement of the $-CH_2CH_2-$ grouping in the polymer backbone with phenylene units to achieve better oxidative stability.

It is expected that all polymers prepared during this study are capable of being crosslinked using silicone technology. The resultant material is an RTV sealant which can be further evaluated both by AFML and Dow Corning in terms of its individual utility as a prototype fuel tank sealant.

SECTION

II. Discussion

A. Fluorosilicone-Fluoroether Hybrid Polymers (FES)

1. Preparation of $X(CF_2)_nO(CF_2)_mY$

Several methods have been investigated with varying degrees of success to prepare functional perfluorocarbon ethers. Thus perfluorooxydiacetic and perfluorooxydipropionic acid fluorides have been prepared by electrochemical fluorination(1). The yields were low but the products could be further reacted to give longer chain polyethers. Perfluorooxydiacetic acid has been prepared(2) from dichloromaleic anhydride using the relatively expensive SF_4 to prepare the intermediate 3,4-dichloroperfluoro-2,5-dihydrofuran(3) which was subsequently oxidized. The addition of perfluoropropylene oxide to a metal fluoride salt of a perfluorocarbon diacid fluoride yields perfluoroethers with acid fluoride functionality(4) but inseparable isomeric mixtures were obtained.

It has been reported(5) that the metal fluoride adduct of perhalocarbonyl compounds will react with fluorine-containing olefins in the presence of halogens to give halogen-containing fluorocarbon ethers. This report prompted an investigation in this laboratory to determine if the reaction could be modified to give α,ω-dihaloperfluorocarbon ethers. The feasibility of this synthetic approach was verified by the preparation of α,ω-dibromoperfluorodiethyl ether starting with bromodifluoroacetyl fluoride(6).

The desirability of this approach to the synthesis of α,ω-difunctional ethers was further emphasized by the fact that the technology to produce the required halo-functional perfluorocarbon acids in large quantities was developed at Dow Corning(7,8).

a. Preparation of $BrCF_2COF$ and $BrCF_2CF_2COF$

Although the starting materials for the preparation of $BrCF_2COF$ and $BrCF_2CF_2COF$ are the corresponding acids, the preparative methods(7,8) more conveniently afford the corresponding esters. These esters were converted to the corresponding acids in good yield with the use of aqueous NaOH. The resulting acids were not exhaustively purified, but rather converted to the corresponding acyl chlorides through the use of PCl_5 or $SOCl_2$. Since KF can be easily prepared in a sufficiently anhydrous state, it proved to be superior to SbF_3 for the conversion of acyl chlorides to acyl fluorides. In one case, ($BrCF_2CF_2COCl$)

an unexpected induction period in the reaction with KF resulted in a partial product loss when the exotherm produced a vigorous refluxing of the product.

$$Br(CF_2)_mCO_2R \xrightarrow[2\text{-}H^+]{1\text{-}OH^-} Br(CF_2)_mCO_2H \xrightarrow[SOCl_2]{PCl_5 \text{ or}} Br(CF_2)_mCOCl$$

m = 1 50-60% overall

m = 2 72.5% overall

$$BrCF_2COCl + SbF_3 \longrightarrow BrCF_2COF \ (>55\%)$$

$$BrCF_2CF_2COCl + KF \longrightarrow BrCF_2CF_2COF \ (88\%)$$

One attempt to produce $BrCF_2COF$ from $BrCF_2CF_2ClBr$ was unsuccessful.

In an attempt to minimize the number of steps involved in the preparation of $BrCF_2CF_2COF$ from $BrCF_2CF_2CCl_3$, reaction of the latter with fuming H_2SO_4 was studied with the intent of isolating $BrCF_2CF_2COCl$ directly from the reaction mixture. It was found that this procedure gave the acid chloride in satisfactory yield but the product contained SO_2 which could not be removed by distillation. However, reaction of the impure $BrCF_2CF_2COCl$ with KF produced $BrCF_2CF_2COF$ which still contained SO_2. It was decided to defer further study of this to a later date rather than risk using an impure starting material in the ether synthesis.

At present, a large quantity (several pounds) of $BrCF_2CF_2COF$ is being prepared using $BrCF_2CF_2COOH$.

b. <u>Preparation of $BrCF_2CF_2OCF_2CF_2(I)$ (Br)</u>

The reaction of perfluoropropionyl fluoride with vinylidene fluoride in the presence of CsF and ICl afforded $CF_3CF_2CF_2OCF_2CH_2I$ in 40% yield(5). This reaction was extended to produce the title compound (Br) in fair yield(6).

$$BrCF_2COF + CsF + CF_2{=}CF_2 + Br_2 \xrightarrow{CH_3CN} BrCF_2CF_2OCF_2CF_2Br$$

b.p. 89-91°C; 22%

During the current contract year the above reaction was repeated and extended using I_2 as the halogen.

$$BrCF_2COF + CsF + CF_2=CF_2 + I_2 \xrightarrow{CH_3CN}$$

$BrCF_2CF_2OCF_2CF_2I$ - 12%

b.p. 64-66°C (110 Torr)

Subsequent work with $BrCF_2CF_2COF$ using D.M.F. as the solvent suggests that the yields of these two ethers could probably be increased by substituting D.M.F. for CH_3CN. In both reactions appreciable quantities of 1,2-dihalotetrafluoroethane were formed. One attempt to produce $BrCF_2CF_2OCF_2CF_2I$ directly from $BrCF_2COF$, ICF_2CF_2I and CsF at 150°C resulted in complete carbonization of the reaction mixture.

c. Preparation of $BrCF_2CF_2CF_2OCF_2CF_2Br$

The title compound was synthesized for several reasons: an unsymmetrical ether was desired as a polymer backbone segment; the method of Evans, et al.(5) was to be further investigated; and the synthesis of the starting acid fluoride ($BrCF_2CF_2COF$) was probably more feasible than the synthesis of $BrCF_2COF$.

The following reaction summarizes the data obtained from this study.

$$BrCF_2CF_2COF + CsF + CF_2=CF_2 + Br_2 \longrightarrow$$

$$BrCF_2CF_2CF_2OCF_2CF_2Br + BrCF_2CF_2OCF_2CF_2Br +$$

recovered acid fluoride

The presence of $BrCF_2CF_2OCF_2CF_2Br$ was not expected and prompted a detailed analysis of the recovered acid fluoride. According to glc/mass spec. analysis the following compounds were present in the amounts indicated: ~ 2% CF_3CF_2Br, ~ 20% $BrCF_2COF$, ~ 65% $BrCF_2CF_2COF$, ~ 12% $BrCF_2CF_2Br$ and a trace of CH_3Br. The presence of $BrCF_2COF$ suggested that the starting $BrCF_2CF_2COF$ be re-examined. G.l.c. analysis of the starting $BrCF_2CF_2COF$ indicated the presence of only one component and derivitization of an aliquot with ethanol yielded only one product according to glc. One can only conclude that the $BrCF_2COF$ was produced during the reaction. It is likely that the observed $BrCF_2CF_2OCF_2CF_2Br$

was produced from the $BrCF_2COF$, but further work is indicated to fully explain these unexpected results. Evans, et al.(5) makes no mention of CF_3CF_2COF yielding CF_3COF or $CF_3CF_2OCF_2CH_2I$ in the presence of CsF, $CF_2=CH_2$ and ICl.

d. Reaction of $BrCF_2CF_2OCF_2CF_2I$ with Hg

A spectrum of products was obtained from the reaction of $BrCF_2CF_2OCF_2CF_2I$ with mercury in the presence of ultraviolet light. Conversions were moderate in the two experiments that were tried. The products were not isolated due to the small scale of the reaction but rather were conveniently characterized by glc/mass spec. as follows:

$\underset{\sim}{1}$	$BrCF_2CF_2OCF_2CF_2CF_2CF_2OCF_2CF_2Br$	~ 83%
$\underset{\sim}{2}$	$BrCF_2CF_2OCF_2CF_2CF_2CF_2OCF_2CF_2I$	~ 12%
$\underset{\sim}{3}$	$BrCF_2CF_2OCF_2CF_2CF_2CF_2CF_2CF_2OCF_2CF_2Br$	~ 3%
$\underset{\sim}{4}$	$BrCF_2CF_2O(CF_2)_4O(CF_2)_4OCF_2CF_2Br$	~ 2%
$\underset{\sim}{5}$	$ICF_2CF_2OCF_2CF_2I$	trace

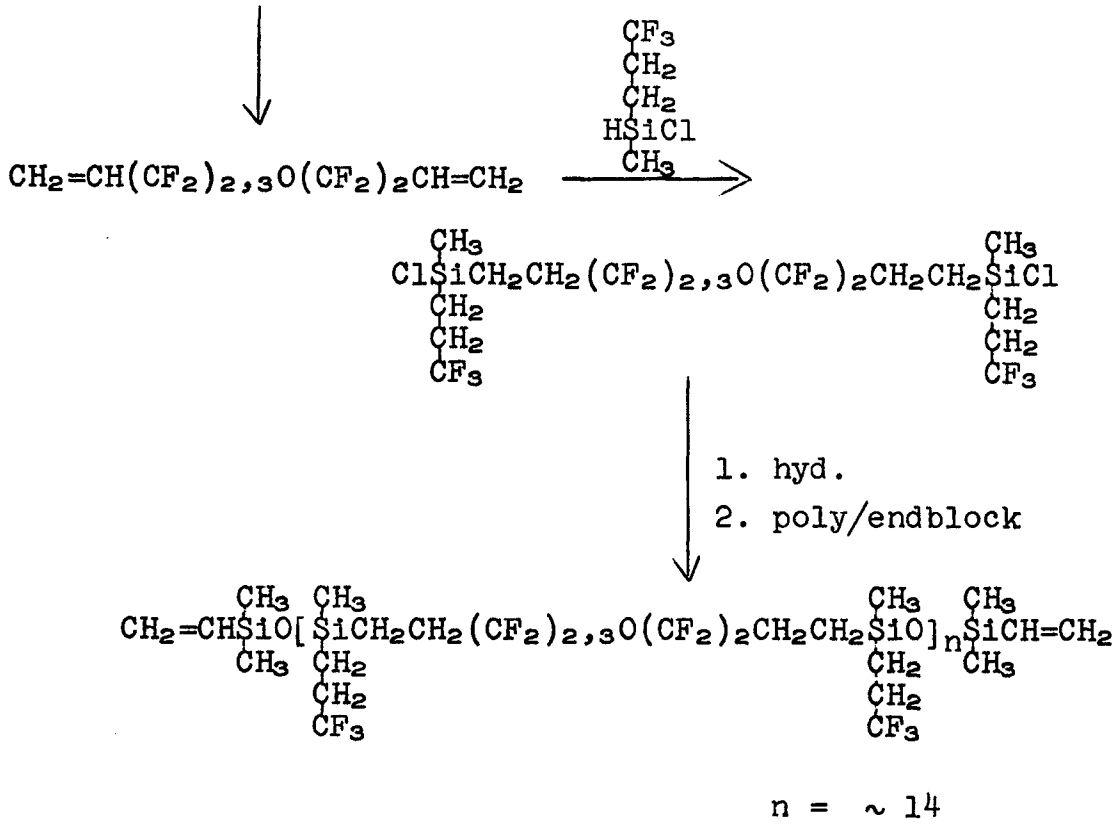
$\underset{\sim}{1}$ is the expected product from $-CF_2I/CF_2I-$ coupling and $\underset{\sim}{3}$ probably arises from the small amount of ICF_2CF_2I initially present. Detection of $\underset{\sim}{4}$ represents the limit of the spectrometer, but higher molecular weight species are probably present only in vanishing small amounts, if at all. The presence of $\underset{\sim}{2}$ and $\underset{\sim}{5}$ suggest that the $-CF_2Br$ group might be participating in the reaction and that iodine-terminated ethers are not required for useful coupling reactions.

2. Preparation of $CH_2=CH(CF_2)_{2,3}O(CF_2)_2CH=CH_2$ and FES Sealant

The synthetic route for the preparation of FES sealant is described in equations below:

$$Br(CF_2)_{2,3}O(CF_2)_2Br + CH_2=CH_2 \xrightarrow{DTBP} BrCH_2CH_2(CF_2)_{2,3}O(CF_2)_2CH_2CH_2Br$$

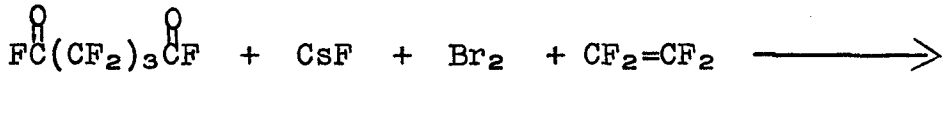
$$\downarrow -HBr$$



The addition of $CH_2=CH_2$ to the mixture of α,ω-dibromoperfluoroether proceeds normally as expected to yield the corresponding diaddition product, $BrCH_2CH_2(CF_2)_{2,3}O(CF_2)_2CH_2CH_2Br$. The yield of $CH_2=CH(CF_2)_{2,3}O(CF_2)_2CH=CH_2$ from $Br(CF_2)_{2,3}O(CF_2)_2Br$ was ~ 33%. With larger scale runs, it is expected to obtain much higher yields. Because of the limited amount of the α,ω-dibromoperfluoroether, the $CH_2=CH_2$ addition had to be recycled four times to convert most of the telogen to the diaddition product. The transformation of the diene to the FES sealant is identical to the procedure described previously(10) for the FCS sealant as shown in equations above. The sealant was found to cure well by a RTV method, and the Tg by D.S.C. is -48°C (-54°F). Formulation and evaluation of the FES sealant is in progress in our sealant TS&D group.

3. Reaction of $FC(CF_2)_3CF$ with $Br_2/CF_2=CF_2/CsF$

A number of attempts to convert perfluoroglutaryl fluoride to a perhalodiether have led only to trace amounts of the desired product (as indicated by glc/mass spec. analysis):



The major (unidentified) products besides $BrCF_2CF_2Br$ appear to be nitrogen-containing compounds (glc/mass spec. analysis). It has been shown that the treatment of labile halides with refluxing D.M.F. gives rise to good yields of displacement products, presumably arising from dimethylamine generated *in situ*:

$$C_6H_5\overset{O}{\overset{\|}{C}}Cl + H\overset{O}{\overset{\|}{C}}N(CH_3)_2 \xrightarrow[4\ hrs.]{150°C} C_6H_5\overset{O}{\overset{\|}{C}}N(CH_3)_2 \quad (13)$$

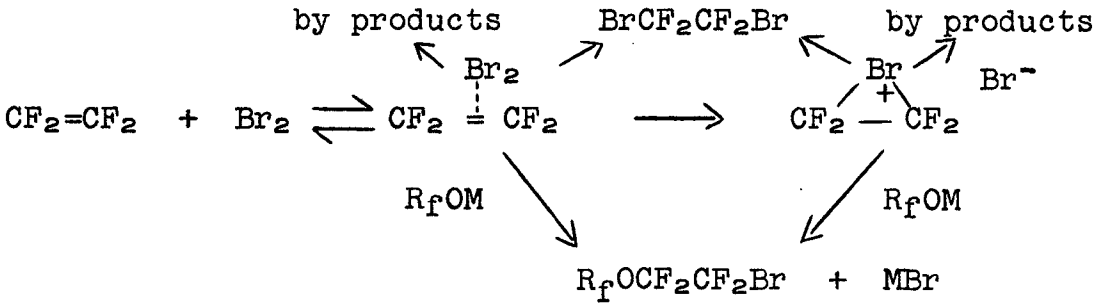
97%

$$C_6F_5CN + H\overset{O}{\overset{\|}{C}}N(CH_3)_2 \xrightarrow[21\ hrs.]{150°C} p\text{-}(CH_3)_2NC_6F_4CN \quad (14)$$

88%

It has also been shown(16) that D.M.F., unless rigorously purified, slowly decomposes to give dimethylamine. It may be reasonably assumed that reaction of perfluoroglutaryl fluoride with dimethylamine is responsible for at least some of the nitrogen-containing products. The use of purified D.M.F. (distilled from P_2O_5) reduced, but did not eliminate, the formation of these side products, and did not improve the previously observed very poor conversion to the desired ether. It is believed that the use of other polar solvents, such as diglyme or acetonitrile will circumvent these difficulties.

A consideration of the reaction mechanism proposed by Evans, *et al.*(5) for ether formation *via* attack of alkoxide on olefins reveals the intermediacy of either a π complex or a bromonium ion:



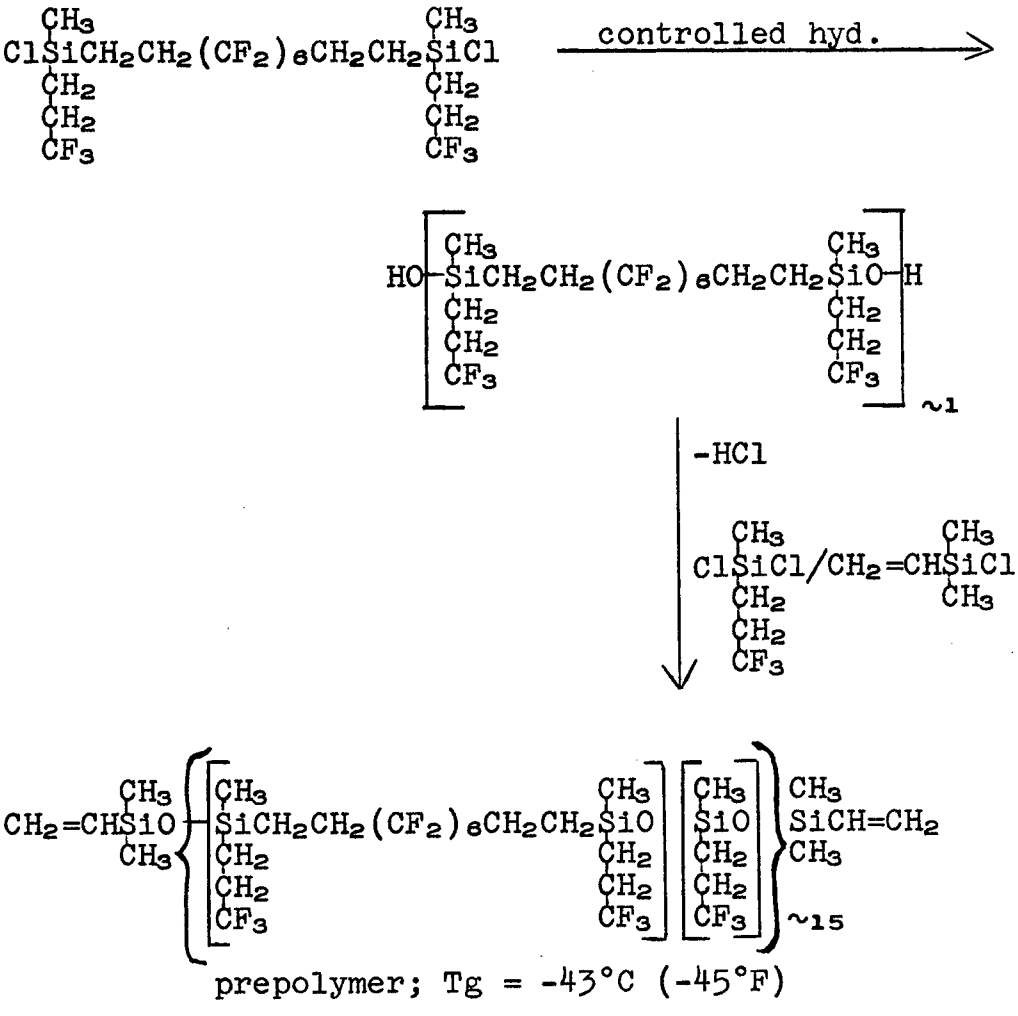
It was felt that the presence of a suitable Lewis acid such as $AlBr_3$ or $AgClO_4$ could intercept the bromide ion and thereby force collapse of the intermediate to the desired product. To this end, the reaction was repeated in the

presence of (impure) $AlBr_3$. A somewhat different product distribution was obtained, but there was no significant increase of the desired fluoroether. It is felt that the competing solvent impurities overrode any possible benefit of the $AlBr_3$. The possibilities of suitable Lewis acids will be evaluated in different solvents.

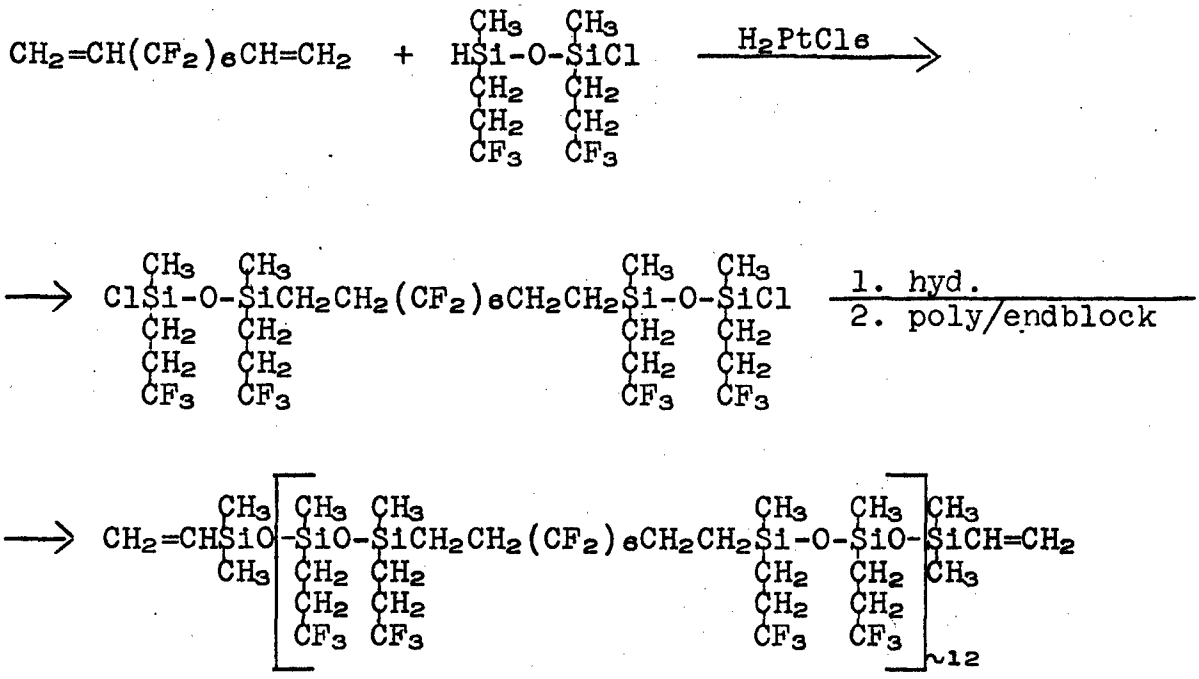
B. FCS-610 Siloxane Copolymer Sealants

Two copolymer sealants were prepared and their synthetic routes are shown in equations below:

Reaction (a)



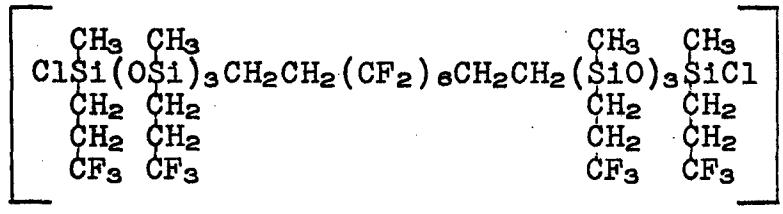
Reaction (b)



Tg = -55°C (-67°F)

The sealants were found to give a satisfactory RTV cure, and preliminary screening these sealants is being conducted in our sealant TS&D group. As shown in reactions (a) and (b) above, a significant improvement of Tg was indeed realized with these copolymer sealants. About one pound of formulated sealant (made by the method (a) above) was submitted to AFML for evaluation.

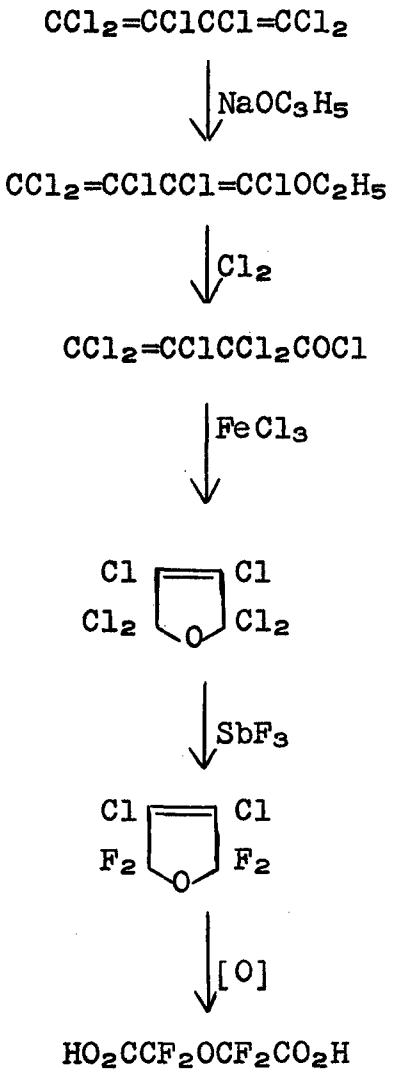
An attempt has been made to prepare



by the reaction of FCS-610 dichloride with $(CF_3CH_2CH_2SiCH_3O)_3$. According to glc analysis of the reaction mixture, it appears that the desired product was formed, however, distillation failed to produce pure product.

C. Preparation of Difunctional Fluorocarbon Ethers From Perchloro-1,3-butadiene

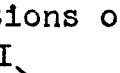
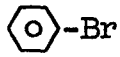
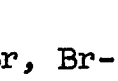
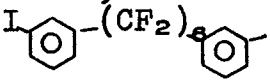
Preparation of the perfluoro-oxydiacetic acid has been accomplished in an overall yield of 42% from the perchlorobuta-1,3-diene as shown in equations below:



An additional quantity, 4 kg., of the perchloro-2,5-dihydrofuran intermediate which can be converted to the perfluorooxydiacetic acid in two steps has been prepared. Small quantities, less than 60 g., of both the perfluoro-oxydiacetyldichloride, $O(CF_2\overset{O}{\overset{\|}{C}}Cl)_2$, and the perfluorooxydi-

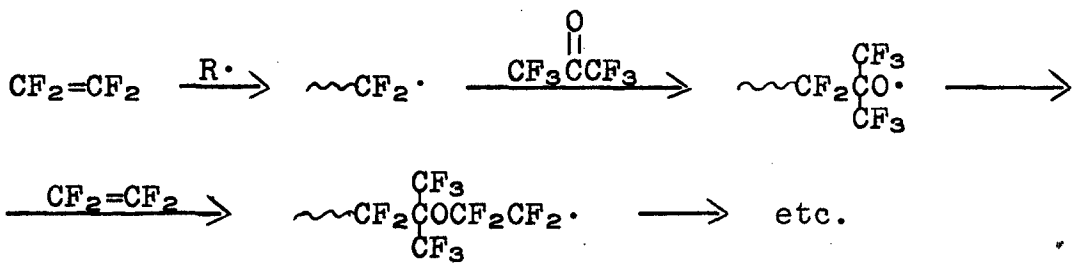
acetyl-difluoride $O(CF_2\overset{O}{\overset{\|}{C}}F_2)_2$, have been prepared with relative ease in initial attempts to evaluate their respective preparative routes.

D. Coupling of $I(CF_2)_xI$ with Aromatic Halides

Coupling reactions of $I(CF_2)_6I$ with  ,  ,  , and were examined. The results of the examinations are summarized in Table II. As the data in Table II show, an extensive reductive dehalogenation occurred. This problem seems to be associated with dimethylformamide used as the solvent. In the future DMSO will be employed as a solvent for this coupling reaction. At present, a small amount of the desired coupled product,  , has been isolated and characterized.

E. Attempted Preparation of Functional Fluoroethers from $(CF_3)_2C{=}O/XCF_2CF_2X/CF_2{=}CF_2$

It has been reported that hexafluoroacetone and tetrafluoroethylene undergo free radical catalyzed copolymerization to yield polyfluoroethers as shown below(11):



On the basis of the above described polyfluoroether forming reaction, the free radical initiated reaction of XCF_2CF_2 (X = Br or I) with $CF_2{=}CF_2/CF_3COCF_3$ was investigated to yield possibly $XCF_2CF_2(CF_2CF_2)_mC(CF_3)_2O(CF_2CF_2)_nX$ and/or $XCF_2CF_2(CF_2CF_2)_nOC(CF_3)_2(CF_2CF_2)_mX$.

In the reaction of $BrCF_2CF_2Br$ with $CF_2{=}CF_2/CF_3COCF_3$, the only isolable product was $(CF_3)_2C(OH)CH_2COCH_3$ formed by Aldol condensation of hexafluoroacetone and acetone derived from the decomposition of di-t-butyl peroxide used as an initiator. Using $BrCF_2CF_2I$ no isolable products were obtained. Thermal reaction of ICF_2CF_2I with $CF_2{=}CF_2/CF_3COCF_3$,

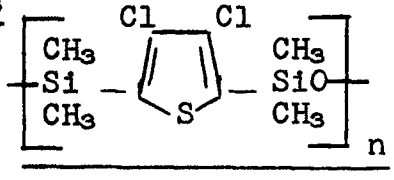
in the absence of a peroxide initiator, gave $I(CF_2)_4I$ and no desired ether. In view of these unsuccessful results, work in this area was immediately discontinued.

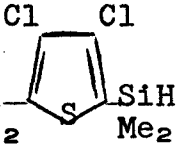
F. Attempted Pyrolysis of Perfluoroethers (Fomblin®, Krytox®, and Freon® E-5) in the Presence of Bromine

Exploratory work has been conducted for the preparation of functionally terminated perfluoroethers from commercially available nonfunctional perfluoroethers. The procedure is to thermally degrade the fluoroether polymer and react the radicals thus formed with excess bromine. The reactions were initially carried out by slowly passing metered amounts of the fluoroether and bromine through a heated nickel reactor tube filled with carborundum spheres and collecting the product in a water scrubber. Results of the reaction at various temperatures are shown in Table I. As the data in Table I show, no significant thermal degradation has occurred. The F^{19} nmr analysis of the product indicates the presence of some CF-Br species. On the basis of the probable structure of the ethers, it appears that CF-Br species were formed by bromination of the hydrogen in -CFH- segment of the ethers. However, a great deal of degradation of perfluoroether occurred with a reactor tube filled with a mixture of ca. 50% alumina and ca. 50% carborundum spheres, but no isolable products were formed.

G. Other Polymer Studies

1. Preparation of





Using a sample of HSi(Me$_2$)– –Si(Me$_2$)H furnished by AFML a polymerization study was conducted by first hydrolyzing the monomer in the presence of 0.2% Pd on carbon followed by condensation with tetramethylguanidine trifluoroacetic acid. Prior to condensation the hydrolyzate was treated with $(CH_2{=}CH)(CF_3CH_2CH_2)SiCl_2$ in order to introduce cross-linking sites. The resultant polymer was a stiff gummy material with a Tg of +3°C (DSC). Analysis by differential thermal means indicates that oxidation begins at 260°C and becomes catastrophic at 480°C. Isothermal gravimetric analysis in air showed a 14% weight loss at 250°C in 24 hours and about 56% weight loss at 316°C. The polymer

seemed to possess some fire retardant properties. A sample of this polymer was submitted to AFML.

2. Attempted Polymerization of $HSi(CH_3)_2-(CF_2)_6-Si(CH_3)_2H$

A sample of the above monomer, obtained from AFML, was hydrolyzed in the presence of Pd/C at room temperature. The reaction proceeded slowly requiring several days to reach completion (absence of SiH). The hydrolyzate was treated with a small amount of tetramethylguanadine/trifluoroacetic acid at 80°C. No evident polymerization took place and analysis of the very complex reaction mixture indicated extensive cleavage of the CF_2-Si bond occurred. Spectral analysis of the reaction mixture indicates the formation of $H(CF_2)_6H$, $(Me_2SiO)_x$ and $H(CF_2)_6Si(CH_3)_2O[Si(CH_3)_2(CF_2)_6(CH_3)_2SiO]_xOSi(CH_3)_2(CF_2)_6H$. Such an extensive decomposition of $\equiv Si(CF_2)_6Si\equiv$ under so mild conditions is unexpected, and our observed instability of $\equiv Si(CF_2)_6Si\equiv$ is quite consistent with the recent findings of Sharp and Coyle(12). The authors report that $CF_3Si\equiv$ gives rise to CF_3H upon treatment with water and that quantitative decomposition of $CF_3Si\equiv$ occurs at temperatures as low as 78°C.

SECTION

III. Experimental

A. Fluorosilicone-Fluoroether Hybrids (FES)

1. Preparation of $BrCF_2CO_2H$

a. Hydrolysis of $BrCF_2CO_2Et$ in Aqueous H_2SO_4

Water, 1,000 ml., containing 100 ml. of conc. H_2SO_4 was stirred with 585 g. (2.88 moles) of ethyl bromodifluoroacetate for 4 hrs. at room temperature and for 64 hrs. at 60°C. An additional 24 hrs. at 60°C failed to consume additional ester. The organic layer (315 g.) was separated and treated with 1,000 ml. of H_2O containing 100 ml. of conc. H_2SO_4 at 60°C for 66 hrs. Insoluble organic material remaining at this point totaled 85 g. The aqueous phases were combined and extracted continuously with ether for 15 days. The dried ether phase was distilled to remove solvent and the residue was fractionated to yield 67 g. (0.33 mole) of nearly pure ester and 164 g. (0.94 mole = 44%) of a liquid/solid product, b.p. 60-62°C (30 mm.). This material was chilled to -10°C and filtered to yield 105 g. (0.6 mole = 28%) of white crystalline $BrCF_2COOH$ and 59 g. (0.34 mole = 16%) of liquid $BrCF_2CO_2H$ (containing some Et_2O).

b. Hydrolysis of $BrCF_2CO_2Et$ in Aqueous NaOH

Ethyl bromodifluoroacetate, 556 g. (2.74 moles) was added slowly to 1,000 ml. of water containing 162 g. (4.05 moles) of NaOH. The cooled reaction mixture was filtered to remove a crystalline phase, 29 g. and the filtrate was devolatilized at reduced pressure to remove ethanol. The aqueous phase was then acidified with 300 g. of conc. H_2SO_4 and continuously extracted with ether for 8 days. Ether was removed by distillation and the residue was fractionated to yield 388 g. (2.22 moles = 81%) of liquid $BrCF_2CO_2H$ (containing some Et_2O).

2. Oxidation of $CF_2BrCFClBr$

A 500 ml. three-necked flask fitted with a stirrer, reflux condenser vented to a dry-ice-cooled trap and an addition funnel was charged with 152 g. (0.55 mole) of $CF_2BrCFClBr$, 13.0 g. (0.044 mole) of $HgSO_4$ and 2.0 g. (0.004 mole) of Hg_2SO_4. Fuming sulfuric acid (30% SO_3), 100 ml. was added dropwise from the addition funnel. When no reaction was noticed the stirred reaction mixture was heated gently overnight. The bromine that was generated and other volatile products were swept into the cold trap

with a stream of nitrogen. The residue was poured into 315 g. of ice and the solution was continuously extracted with ether for 10 days. No organic material could be isolated from this extract. The volatile material was swept through a solution of 67.5 g. (0.8 mole) of hexene-1 in 610 g. of CCl_4 to absorb halogen. G.l.c. analysis detected the presence of only one product (in addition to unreacted hexene) in the CCl_4 phase, presumably 1,2-dibromohexane.

3. Preparation of $BrCF_2COCl$

Crystalline $BrCF_2COOH$, 105 g. (0.6 mole) was melted and added slowly to 150 g. (0.72 mole) of stirred PCl_5 contained in a 500 ml., three-necked flask. The reaction mixture was stirred at room temperature overnight, distilled to a vapor temperature of 70°C and the distillate fractionated at atmospheric pressure with a 15" glass helices packed column to give glc pure $BrCF_2COCl$, 47.0 g. (0.242 mole = 40.5%), b.p. 49-50°C, infrared 5.49 μ, 5.58 μ (-COCl). The reaction was repeated with 388 g. of liquid $BrCF_2COOH$ (containing some Et_2O), and 454 g. of PCl_5 to give 209 g. of product that contained ca. 10% Et_2O. Another portion of liquid $BrCF_2COOH$ (containing some Et_2O), 59 g. was treated with 100 ml. of $SOCl_2$ containing 0.5 ml. of wet pyridine and the product fractionated to give 45.5 g. of a 1:2 mixture of Et_2O and $BrCF_2COCl$. The volatile material that was trapped beyond the receiver during the fractionations described above was refractionated to give 136 g. (0.7 mole) of $BrCF_2COCl$. Total product equalled 437 g. which was approximately 85% pure.

4. Preparation of $BrCF_2COF$

A two-liter, three-necked round-bottom flask was fitted with a stirrer, water cooled condenser and isobaric addition funnel vented to two dry ice cooled traps in series. Antimony trifluoride, 600 g. (3.37 moles) was placed in the flask and $BrCF_2COCl$, 437 g. (containing some ether) was added slowly *via* the funnel. No exotherm was noticed so the reaction mixture was stirred at reflux overnight. The volatile product was fractionated through a 15" glass helieces packed column and transferred *via* vacuum line techniques to a metal cylinder, to yield 219 g. (1.24 moles = 25% based on $BrCF_2CO_2Et$) of $BrCF_2COF$. An infrared spectrum of the gas showed a sharp absorption at 5.30 μ (-COF) and crude vapor pressure measurements at -78°C, -15°C and 0°C indicated a normal boiling point of -3°C ± 1°C.

5. Preparation of $CCl_3CF_2CF_2Br$

Telomerization of $CF_2=CF_2$ in the presence of CCl_3Br gave $CCl_3CF_2CF_2Br$ in a yield greater than 75%(9).

6. Preparation of $BrCF_2CF_2COOCH_3$

Following the reported method(8), the ester, $BrCF_2CF_2COOCH_3$, was prepared in an average of 75% yield.

7. Preparation of $BrCF_2CF_2COCl$

a. From $BrCF_2CF_2COOMe$

To a warm solution of 216 g. (5.4 moles) of NaOH in one liter of water was added 863 g. (3.6 moles) of $BrCF_2CF_2CO_2Me$, at room temperature overnight. Methanol was removed through a Vigreaux column at minimum pressure and the aqueous residue was treated cautiously with 530 g. (5.4 moles) of concentrated H_2SO_4. The heavy organic layer, 918 g., was separated and extracted with ether. The aqueous layer was extracted continuously with ether for three days. The combined ether extracts were dried (Drierite) and devolatilized to yield 830 g. of a liquid product, which was added to 900 g. (4.33 moles) of PCl_5 contained in a three liter, three-necked flask. After standing at room temperature overnight, the reaction mixture was distilled through a Vigreaux column to a pot temperature of 100°C. The distillate was fractionated through a 36" spinning band column to yield 634.7 g. (2.61 moles = 72.5%) of $BrCF_2CF_2COCl$, b.p. 66.5-69.5°C. The spectral properties were completely in agreement with the assigned structure.

b. From $BrCF_2CF_2CCl_3$ via $BrCF_2CF_2COOH$

A three liter, three-neck flask fitted with a mechanical stirrer, one liter isobaric dropping funnel, and water-cooled condenser vented to a dry ice/acetone-cooled trap was heated thoroughly with a hot air gun and swept with dry nitrogen. After cooling, it was charged with 9 g. of Hg_2SO_4, 45 g. of $HgSO_4$, and 900 g. (3 moles) of $Cl_3CCF_2CF_2Br$. About 900 ml. of 30% fuming sulfuric acid was added rapidly dropwise to the stirred solution, and the mixture was maintained at about 115° for 76 hours.

The dark reaction mixture was cooled to room temperature, and the salt was filtered off. The filtrate was added dropwise to ice water contained in a five liter flask

fitted with a stirrer and cooled in an ice bath. About 400 g. of a heavy strong-smelling organic liquid separated and was dried over Drierite; the aqueous phase was continuously extracted with ether for four days. The ether extract was dried over Drierite, and the ether was stripped off. The residue was combined with the organic layer to give a total of 450 g. of crude acid. The crude acid was converted to $BrCF_2CF_2COCl$ following the procedure described above.

8. Preparation of $BrCF_2CF_2COF$

a. Neat

Dry KF, 25 g. (0.43 mole) was treated with 68.2 g. (0.28 mole) of $BrCF_2CF_2COCl$ in a 250 ml., three-necked flask that had been fitted with a stirrer and reflux condenser vented to a Dry Ice cooled trap. A slight exotherm was noted; gentle heating caused a reflux. The condenser water was turned off and the product allowed to escape to the trap, yielding 55.3 g. (0.246 mole = 87.8%) of $BrCF_2CF_2COF$. The reaction was repeated by adding 200 g. (3.45 moles) of dry KF in five portions over a period of five minutes to 566.5 g. (2.33 moles) of $BrCF_2CF_2COCl$ contained in a one liter, three-necked flask. Shortly after the final portion had been added an exothermic reaction occurred which caused a flooding of the condenser, the popping of a stopper and a partial loss of product. The product, 355 g. (1.58 moles = 67%) was found to be slightly contaminated by acid chloride according to glc and infrared analyses. The products from both fluorinations were combined and fractionated in 18" glass helices packed column to give 350 g. (1.57 moles = 60%) of $BrCF_2CF_2COF$, b.p. 29-30°C. The infrared spectrum showed a strong band at 5.35 μ (-COF).

b. With Solvent

An oven dried (120°, 2 hrs.) three-necked 100 ml. flask was fitted with a stirrer, dropping funnel, and distillation head, and charged with 21 g. (about 360 mmoles) of technical grade dried (210°/0.2 mm.) anhydrous potassium fluoride. The system was flushed with dry nitrogen and heated to 180° for 2 hrs. After cooling, 50 ml. of acetonitrile which had been dried over molecular sieves was added. The suspension was heated to about 60° and 22 g. (90 mmoles) of $BrCF_2CF_2COCl$ was added slowly. A low boiling fraction, shown to consist of $BrCF_2CF_2COF$

(infrared identical to that of an authentic sample) and acetonitrile was collected. The total yield of pure product was 15.9 g. (70 mmoles, 78%).

9. Preparation of $BrCF_2CF_2COCl$ Directly from $CCl_3CF_2CF_2Br$

Into a stirred mixture (slurry) of 300 g. (1.05 moles) of $CCl_3CF_2CF_2Br$, 15 g. of $HgSO_4$, and 3 g. of Hg_2SO_4 was added 300 ml. of fuming H_2SO_4 (30% SO_3) at room temperature. After the addition, the reaction was stirred at 125°C for 72 hrs. under a mild reflux. The reaction mixture was then strip distilled under atmospheric pressure at a pot temperature up to 130°C to yield ca. 187 g. of a light reddish liquid. Gas chromatographic analysis indicates that the product is a mixture of two components. A small amount of the strip distillate was treated with ethanol. Gas chromatographic and infrared analyses showed that the product arising from the ethanol treatment is $BrCF_2CF_2COOC_2H_5$, thus indicating that one of the two components in the strip distillate contains the $BrCF_2CF_2\overset{O}{\overset{\|}{C}}-$ moiety, probably derived from $BrCF_2CF_2COCl$.

Redistillation of the strip distillate gave 151 g. of liquid product, b.p. 61-67°C. The redistilled material was again composed of one major compound and a minor impurity. Glc-mass spec. and infrared analyses indicate that the major component is $BrCF_2CF_2COCl$ and the minor impurity is SO_2. Therefore, it appears that it would be difficult to separate $BrCF_2CF_2COCl$ from SO_2 contamination.

10. Preparation of $BrCF_2CF_2COF$ from $BrCF_2CF_2COCl$ Containing SO_2 as an Impurity

About 136 g. of $BrCF_2CF_2COCl$ containing SO_2 as an impurity was added to 44 g. of anhydrous KF with stirring at room temperature. Upon the initial addition, a mild exothermic reaction occurred. The addition was conducted slowly for ca. 1 hr. while stirring under an atmosphere of nitrogen. The reaction was then stirred at 65°C over a week-end, but a considerable amount of high boiler remained in the reaction flask (b.p. of $BrCF_2CF_2COF$ is 29-30°C). Then, the reaction temperature was raised to 80-90°C, and an additional 25 g. of anhydrous KF was introduced to the stirred reaction mixture. After ca. 0.5 hr. of induction, a liquid material was collected in the receivers cooled to 0°C and -78°C. The product collected in the receiver cooled to 0°C, ca. 20 g., was

distilled to yield a gas chromatographically pure product b.p. $<30°C$. Infrared spectrum of the product was identical in every detail with that of known $BrCF_2CF_2COF$ (made from pure $BrCF_2CF_2COOH$) with the expection that the spectrum has a strong band at ca. 1415 $cm.^{-1}$ that is absent in the spectrum of known $BrCF_2CF_2COF$. Therefore, this direct approach for the synthesis of $BrCF_2CF_2COCl(F)$ is being temporarily abandoned until a better purification procedure is available. At present, $BrCF_2CF_2COF$ is being prepared through $BrCF_2CF_2COOH$.

The residue in the still pot after strip distillation was treated with ethanol to yield 69 g. of $BrCF_2CF_2COOC_2H_5$ (ca. 90% pure by glc).

11. Preparation of $BrCF_2CF_2OCF_2CF_2Br$

A heavy-walled glass ampoule of 260 ml. capacity was charged with 15.9 g. (0.105 mole) of CsF and 50.3 g. of dry (P_2O_5) CH_3CN. The ampoule was chilled to -78°C and further charged with 16.0 g. (0.10 mole) of bromine and 17.7 g. (0.10 mole) of $BrCF_2COF$ using vacline techniques. The ampoule was then warmed to -15°C and pressurized to 0 psig. with $CF_2=CF_2$ (no precautions taken to remove the inhibitor). A pressure drop was noticed so further $CF_2=CF_2$ addition was conducted as follows:

+ 10 psig. to -10 psig./-15°C to +10°C/overnight		
+ 10 psig.	/30°C	/4 hrs.
+ 15 psig.	/27°C	/3 days

Bromine color was discharged and 120% of theoretical $CF_2=CF_2$ was used. The reaction mixture was filtered to give 20.0 g. of salts and a filtrate which was quenched with water. The insoluble phase was washed with one equal volume portion of water, dried with Drierite, filtered and fractionated at atmospheric pressure on a spinning band column to yield 8.3 g. (0.022 mole = 22%) of glc pure $BrCF_2CF_2OCF_2CF_2Br$, b.p. 89-91°C, whose infrared spectrum was identical with an authentic sample prepared independently(6), $n_D^{25} = 1.3291$; F^{19} nmr 69.9 ppm (triplet, 4.02, CF_2Br), 87.0 ppm. (triplet, 3.98, CF_2O).

Anal. calc'd. for $C_4Br_2F_8O$: C, 12.70; Br, 42.52; F, 40.44. Found: C, 12.9; Br, 42.5; F, 40.8.

12. Preparation of $BrCF_2CF_2OCF_2CF_2I$

A heavy-walled glass ampoule of 260 ml. capacity was charged with 28.6 g. (0.176 mole) CsF and dried *in vacuo* overnight at 150°C. The vacuum was broken with dry (Drierite) nitrogen and the tube was charged with 90.9 g. of dry $(P_2O_5)CH_3CN$, 33.8 g. (0.191 mole = 8.6% excess) of $BrCF_2COF$, and 90 g. (0.355 mole = 102% excess) of pulverized I_2. The evacuated ampoule was pressurized to 15 psig. with $CF_2=CF_2$ at room temperature and the reaction allowed to continue for 40 hrs. while being agitated with a wrist-action shaker. Volatile material was removed from the ampoule at minimum pressure and collected in a dry ice cooled trap. Iodine was removed from the distillate with aqueous sodium thiosulfate and the colorless organic layer was washed with one portion of water and one portion of aqueous $NaHCO_3$. Fractionation of the dried (Drierite) organic layer on an 18" spinning band column at reduced pressure afforded 9.0 g. (0.021 mole = 12%) of glc pure $BrCF_2CF_2OCF_2CF_2I$, n_D^{29} = 1.3622, b.p. 64-66°C (110 Torr); F^{19} nmr 64.4 ppm. (triplet, 2.0, CF_2I), 69.5 ppm. (triplet, 2.1, CF_2Br), 87.0 ppm. (complex, 4.0, CF_2OCF_2). Molecular weight = 422 (mass spec.), calculated for C_4F_8BrIO = 423, and 6.1 g. of an intercut consisting of equal molar amounts of $BrCF_2CF_2OCF_2CF_2I$ and ICF_2CF_2I which was identified by concurrent glc, F^{19} nmr, 52.4 ppm. (singlet, ICF_2CF_2I) and glc/mass spec. (m.w. = 354, calc'd. = 354).

13. The Reaction of $BrCF_2COF$ with ICF_2CF_2I

A heavy walled glass ampoule (20 cm. x 2.0 cm. o.d.) was charged with 6.5 g. (0.037 mole) of $BrCF_2COF$, 22.8 g. of dry (P_2O_5) D.M.F., 5.10 g. (0.034 mole) of dry (heat, vacuum) CsF and 12.0 g. (0.034 mole) of ICF_2CF_2I. The ampoule was chilled to -78°C, evacuated and sealed. After being heated and rocked at 150°C for 16 hrs., the tube was chilled to -78°C, opened and vented to a dry ice cooled trap. Considerable pressure release occurred when the ampoule was opened and 2.4 g. of a gas was lost. Very little material was collected in the trap while the ampoule was being warmed to room temperature. Quenching the devolatilized reaction mixture with aqueous Na_2SO_3 solution did not precipitate any organic phase or discharge the dark color of the material. Filtration yielded a carbonaceous residue which was not examined further.

14. Preparation of $BrCF_2CF_2CF_2OCF_2CF_2Br$

A two-liter, one-necked flask fitted with a magnetic stirring bar was charged with 152 g. (1.0 mole) of CsF and dried *in vacuo* for several hours at 140°C. The vacuum was broken with dry nitrogen and 400 ml. of dry $(P_2O_5)CH_3CN$ was added to the salt. The slurry was chilled in ice water and treated with a solution of 228.8 g. (1.008 moles) of $BrCF_2CF_2COF$ in 300 ml. of dry $(P_2O_5)CH_3CN$. Gentle warming and stirring eventually resulted in a clear solution. The solution was chilled in ice water and treated with 176 g. (1.1 moles) of Br_2. The air above the liquid was purged using $CF_2=CF_2$, the flask closed with a stopper containing a dip tube (just above the surface of the reaction mixture) and the system pressurized to 5 psig. with $CF_2=CF_2$ overnight as the temperature increased from 0° to approximately 20°C. After 16 hrs., all bromine had been consumed and 103% of theoretical $CF_2=CF_2$ was used. In addition, considerable salt had precipitated. Glc analysis suggested the presence of solvent, CF_2BrCF_2Br and unreacted $BrCF_2CF_2COF$ but none of the desired product. An aliquot was washed with water and the organic phase was found to be $BrCF_2CF_2Br$ according to glc analysis. The reaction mixture was distilled at 30 mm. until the distillate began to freeze in the dry ice cooled trap, indicating that solvent was being removed. Fractionation of the distillate on a 36" spinning band column gave 174 g. (76%) of starting acid fluoride, b.p. 27-30°C, and 76 g. (27.5%) of $BrCF_2CF_2Br$.

The reaction was repeated in an ampoule of 260 ml. capacity using 23.0 g. (0.151 mole) of dry (heat and vacuum) CsF, 35.0 g. (0.154 mole) of $BrCF_2CF_2COF$, 80 ml. of dry (P_2O_5) D.M.F. and 26.5 g. (0.166 mole = 10% excess) of bromine. The evacuated ampoule was pressurized with $CF_2=CF_2$ to 5 psig. and agitated at room temperature for 16 hrs. Bromine color was discharged and salts precipitated. The reaction was distilled under reduced pressure at room temperature to 1/2 of its volume and the distillate was fractionated to yield 7.7 g. (0.034 mole = 22%) of $BrCF_2CF_2COF$, b.p. 29-31°C, 22.4 g. (0.0525 mole = 43.7% yield) of $BrCF_2CF_2CF_2OCF_2CF_2Br$, b.p. 112-114.5°C; and 6.8 g. (0.026 mole) of $BrCF_2CF_2Br$, b.p. 45-47°C, whose infrared spectrum was identical with that of an authentic sample.

Anal. calc'd. for $C_5F_{10}Br_2O$: C, 14.10; Br, 37.53; F, 44.61; m.w. = 426. Found: C, 14.1; Br, 34.8; F, 46.7; m.w. = 424.

The F^{19} nmr spectrum was consistent with the assigned structure, $BrCF_2CF_2CF_2OCF_2CF_2Br$.

In addition, a 3.6 g. intercut was obtained which, according to glc/mass spec. contained $BrCF_2CF_2OCF_2CF_2Br$ and $BrCF_2CF_2CF_2OCF_2CF_2Br$.

Subsequent reactions were conducted in D.M.F. using either glass ampoules or a Parr kettle. Since the experimental technique is essentially the same in each case a tabular summary of all the reactions will suffice to describe the results. In some runs recovered $BrCF_2CF_2COF$ was used as the starting material. Several attempts were made to free this material of the impurities, $BrCF_2CF_2Br$, CF_3CF_2Br, and $BrCF_2COF$, but prohibitive losses of $BrCF_2CF_2COF$ in intercuts was experienced. In summary, from 350 g. (1.57 moles) of $BrCF_2CF_2COF$ there was obtained 118.4 g. (0.28 mole = 17.7%) of pure $BrCF_2CF_2CF_2OCF_2CF_2Br$, b.p. 114°C and 117.3 g. of an approximately equimolar mixture of $BrCF_2CF_2OCF_2CF_2Br$ and $BrCF_2CF_2CF_2OCF_2CF_2Br$, i.e., ca. 55 g. (0.15 moles = 9.5%) of $BrCF_2CF_2OCF_2CF_2Br$ and ca. 63 g. (0.15 mole = 9.5%) of $BrCF_2CF_2CF_2OCF_2CF_2Br$. Total yield of ethers (assuming both ethers arise from $BrCF_2CF_2COF$) was 36.7%. A detailed summary of these reactions can be found in Table III.

15. The Reaction of $BrCF_2CF_2OCF_2CF_2I$ with Mercury

A small quartz ampoule was charged with 31 g. (0.15 g.-atom) of mercury and 2.2 g. (0.005 mole) of $BrCF_2CF_2OCF_2CF_2I$. The ampoule was sealed and heated at 85°C for 8 hrs. while being rocked end-to-end. No apparent reaction occurred so the unopened ampoule was rocked at a distance of 10 cm. from a 100 Watt high pressure Hanovia U.V. light for 16 hrs. The tube was opened, extracted with ether, filtered, the filtrate concentrated on a steam bath, filtered, and examined by glc. Starting material (~ 50%) and higher boiling materials (~35%) were detected. The coupling reaction was repeated using a quartz tube (4 cm. x 30 cm.) sealed at one end and containing a glass stirring rod and Teflon® paddle inserted through a rubber stopper. The tube was charged with 238 g. (1.2 g.-atom) of Hg, purged with dry N_2 while being heated to remove residual H_2O and finally stoppered. When cool, the tube was charged with 6.58 g. (0.0155 mole) of $BrCF_2CF_2OCF_2CF_2I$ and the mixture rapidly stirred for 24 hrs. at a distance of 10 cm. from a 100 Watt Hanovia U.V. light source. Glc analysis indicated a cleaner but less complete reaction than was observed previously. The reaction mixture

was extracted with CH_2Cl_2, filtered, concentrated, and combined with the product from the first reaction. This combined product was examined by glc/mass spec. Molecular ion peaks were observed for the several glc peaks, indicating the following species to be present:

[(%) = glc area % of product]: $BrCF_2CF_2OCF_2CF_2I$, m.w. = 422, calc'd. m.w. = 423; $BrCF_2CF_2O(CF_2)_4OCF_2CF_2Br$, (83%) m.w. = 590; calc'd. m.w. = 592; $BrCF_2CF_2O(CF_2)_4OCF_2CF_2I$, (12%) m.w. = 638; calc'd. m.w. = 639; $BrCF_2CF_2O(CF_2)_6OCF_2CF_2Br$, (3%) m.w. = 690; calc'd. m.w. = 692 (probably arising from the incorporation of some ICF_2CF_2I impurity); and calc'd. m.w. = 808; $BrCF_2CF_2O(CF_2)_4(CF_2)_4OCF_2CF_2Br$, (2%) m.w. = 806.

A bromine free compound with a m.w. = 470 was detected eluting concurrently with $BrCF_2CF_2O(CF_2)_4OCF_2CF_2Br$. Calc'd. for $ICF_2CF_2OCF_2CF_2I$, m.w. = 470.

16. Addition of Ethylene to α,ω-Dibromoperfluoroether

About 129 g. (0.32 mole) of a mixture of $BrCF_2CF_2OCF_2CF_2Br$ (ca. 60%) and $BrCF_2CF_2OCF_2CF_2CF_2Br$ (ca. 40%) and 2.3 g. (ca. 5 mole %) of di-t-butyl peroxide were charged to ca. a 250 ml. capacity glass pressure reactor equipped with a stirrer and means to measure pressure. The system was flushed with ethylene, pressurized with ethylene, and allowed to react a 125-130°C with stirring, under a constant ethylene pressure of ca. 20 psi. The reaction was stopped at the end of 7 hrs., an additional 2.3 g. of di-t-butyl peroxide was introduced to the reaction mixture, and the reaction was continued for an additional 7 hrs. Gas chromatographic analysis of the mixture indicates ca. 63% conversion of starting ethers, ca. 73% yield of 1:1 adducts, $BrCH_2CH_2(CF_2)_xO(CF_2)_yBr$, and ca. 19% yield of 1:1:1 adducts, $BrCH_2CH_2(CF_2)_xO(CF_2)_yCH_2CH_2Br$ (x = 2 or 3 and y = 2). The reaction mixture was distilled to yield the following fractions:

Cut	b.p.	wt.	glc
1	up to 72°C	3 g.	
2	72° - ca. 50°C/15 mm.	90 g.	starting ether and 1:1 adducts
3	still pot		mostly 1:1:1 adducts

The cut no. 2 was again reacted with ethylene in the presence of di-t-butyl peroxide in the same manner described above. This process of ethylene addition/stripping has been repeated four times and the combined crude 1:1:1 adduct was distilled to yield 52 g. (~ 52% yield), b.p. 45-74° (0.75 mm.) of ca. 80% pure $BrCH_2CH_2(CF_2)_{2,3}O(CF_2)_2CH_2CH_2Br$ (2 = ~ 60% and 3 = ~ 40%). In addition to the product, about 40 g. (ca. 31% recovery) of starting material and some 1:1 adducts were isolated.

Since the 1:1:1 adduct was impure, no analysis was obtained on it. However, a complete analysis was made on $CH_2=CH(CF_2)_{2,3}O(CF_2)_2CH=CH_2$ after dehydrobromination of the 1:1:1 adduct.

17. Preparation of $CH_2=CH(CF_2)_{2,3}O(CF_2)_2CH=CH_2$

To a stirred solution of 25 g. (0.446 mole) of KOH in 100 ml. of ethanol 52 g. of ca. 80% pure $BrCH_2CH_2(CF_2)_{2,3}O(CF_2)_2CH_2CH_2Br$ was added slowly at room temperature; a mild exothermic reaction occurred. After the reaction mixture was stirred overnight at room temperature, about 400 ml. of water was introduced to the mixture to dissolve the salt formed. The organic layer (bottom) was separated and dried over Drierite to yield ~ 30 g. of a crude product. Distillation of the crude product gave the following fractions:

n_D^{26}	cut	b.p.(°C)	wt. (g.)	$CH_2=CH(CF_2)_xO(CF_2)_2CH=CH_2$
	1	76-119	1.2	
1.3194	2	119	3.0	x = 2
	3	119	7.3	x = 2
	4	119-140	3.0 (22.5)	x = 2 and 3
1.3190	5	140	4.0	x = 3
	6	140	5.2	x = 3
	7	still residue	6.5	

The overall yield of $CH_2=CH(CF_2)_{2,3}O(CF_2)_2CH=CH_2$ from $Br(CF_2)_{2,3}O(CF_2)_2Br$ is about 33%. The physical and spectral properties of $CH_2=CH(CF_2)_2O(CF_2)_2CH=CH_2$ were identical to those of the diene-ether prepared previously from $FOCCF_2CF_2OCF_2CF_2COF$ (AFML-TR-70-278, Part I). The infrared and F^{19} nmr spectra of the cuts 5 and 6 were consistent with $CH_2=CH(CF_2)_3O(CF_2)_2CH=CH_2$.

Anal. calc'd. for $C_9H_6F_{10}O$: C, 33.76, H, 1.89. Found: C, 33.96; H, 1.91.

18. Preparation of $ClSi(CH_3)(CF_3CH_2CH_2)CH_2CH_2(CF_2)_{2,3}O(CF_2)_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiCl$

A mixture of 20 g. (~ 0.068 mole) of $CH_2=CH(CF_2)_{2,3}O(CF_2)_2CH=CH_2$ (2 = ~ 60% and 3 = ~ 40%), 120 g. (0.68 mole) of $(CF_3CH_2CH_2)CH_3SiHCl$, and 2.5 g. (~ 2.5% of silane) of di-t-butyl peroxide was heated with stirring under a mild reflux and atmosphere of nitrogen (the reaction temperature = ~ 105°C). At the end of 24 hrs. of the reaction, gas chromatographic analysis indicated that the reaction was completed. After removal of the excess silane, the residue was distilled to give 27 g. (61% yield) of pure

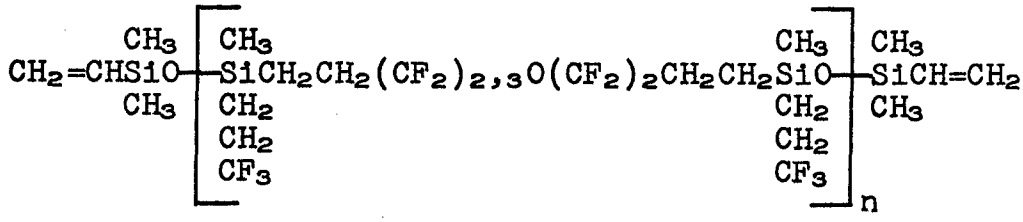
$$\begin{array}{l} CH_3 \\ ClSiCH_2CH_2(CF_2)_{2,3}O(CF_2)_2CH_2CH_2SiCl, \\ CH_2 \\ CH_2 \\ CF_3 \end{array} \quad \begin{array}{l} CH_3 \\ \\ \\ CH_2 \\ CH_2 \\ CF_3 \end{array}$$ b.p. 152° (1 mm.).

The spectral (infrared, H^1, and F^{19} nmr) properties were completely in agreement with the assigned structure. Elemental analysis is in progress.

19. Hydrolysis and Polymerization of $ClSi(CH_3)(CF_3CH_2CH_2)CH_2CH_2(CF_2)_{2,3}O(CF_2)_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiCl$

Into a stirred mixture of 17 g. (~ 100% excess) of $NaHCO_3$ in 200 ml. of water and 50 ml. of ether was added a solution of 22 g. (~ 0.034 mole) of the title chlorosilane in 100 ml. of ether at room temperature. Then, the reaction mixture was stirred for 6 hrs. at room temperature. The ether layer was separated and dried over Drierite. After removal of ether, the resulting hydrolyzate was kept under a high vacuum at room temperature over a week-end and then treated with 0.59 g. (0.0049 mole) of $CH_2=CH(CH_3)_2SiCl$

with stirring at 80°C for 8 hrs. During the reaction, the reaction system was continuously purged with nitrogen. The reaction mixture was dissolved in ether, washed with aqueous $NaHCO_3$, and dried over Drierite. After removal of ether, the resulting prepolymer was then mixed with 3 drops of tetramethylguanidine-trifluoroacetic acid, and the mixture was stirred at 80°C for 15 hrs. under a high vacuum. The fluid polymer was dissolved in ether, washed with aqueous $NaHCO_3$, and dried over Drierite. The ether was removed in vacuo, and the resulting fluid was stripped at 150°C under ~ 0.1 mm. Hg to yield 18 g. of sealant consistency fluid polymer of the structure:



H^1 nmr analysis indicates n is equal to ~ 15. The Tg of the uncured polymer was found to be -48°C (-54°F, by D.S.C.). The polymer was found to cure well by RTV method and is being formulated in our sealant TS&D group.

20. Preparation of Perfluoroglutaryl Fluoride

A two liter, three-necked flask was oven dried at 115° for 2 hrs. While still warm, it was fitted with a stirrer and distillation head vented to a dry ice/acetone trap, and purged with dry nitrogen. About 175 g. (3 moles) of anhydrous KF which had been dried under vacuum (180°/0.2 mm.) overnight was added to the reaction flask, which was then heated to 180° for 1 hr. After cooling, about 800 ml. of diglyme which had been heated with lithium aluminum hydride was distilled directly into the flask. The slurry was heated to 125° and 234 g. (846 mmoles) of perfluoroglutaryl chloride was added dropwise; pure perfluoroglutaryl fluoride was collected (172 g., 704 mmoles, 83% yield). The infrared (C=O 5.3 μ) and mass spectrum (M^+ = 244) were consistent with the assigned structure.

21. Reaction of Perfluoroglutaryl Fluoride with CsF, $CF_2=CF_2$ and Br_2 in D.M.F.

A heavy wall 260 ml. glass ampoule was charged with 23.0 g. (151 mmoles) of CsF and heated under vacuum (165°/0.35 mm.) overnight. The vacuum was broken with dry

nitrogen, and the ampoule was fitted with a septum which was topped by a syringe needle attached to a drying tube filled with Drierite. The ampoule was cooled in dry ice/acetone, and 130 ml. of D.M.F. (dried over molecular sieves) was injected via a syringe, followed by 18.3 g. (75 mmoles) of perfluoroglutaryl fluoride. The ampoule was warmed to room temperature and shaken on a wrist action shaker for several hours, but only a small amount of CsF dissolved.

The mixture was cooled to -10° and 30.5 g. (190 mmoles) of bromine was added. The ampoule was warmed to room temperature and then connected to a vacuum line, after which it was cooled to -78° and evacuated again, and then pressurized to 0 psig. with tetrafluoroethylene. Upon reaching room temperature, the ampoule was pressurized to 5 psig. with shaking. Within 3 hrs., the mixture had become homogeneous, but still retained the bromine color. A 5-10 psig. pressure was maintained until no further pressure drop was observed.

The reaction mixture was poured into dry methanol to esterify an acyl fluorides present. Glc/mass spec. analyses of the mixture showed the presence of approximately equimolar amounts of $BrCF_2CF_2Br$ and $MeO_2(CF_2)_3CO_2Me$, in addition to a trace amount of the desired ether, $BrCF_2CF_2O(CF_2)_5OCF_2CF_2Br$, and three other products probably containing amide linkages (postulated to arise from reaction of solvent impurities with perfluoroglutaryl fluoride).

Repetition of this reaction using D.M.F. distilled from P_2O_5 led to a somewhat similar product distribution with the exception of one new peak; the mixture is presently being analyzed by glc/mass spec.

Repetition of this reaction under essentially identical conditions in the presence of about 190 mmoles of impure $AlBr_3$ led to the isolation of $BrCF_2CF_2Br$ and a small amount of an intractable oil.

B. FCS-610/Siloxane Copolymer Sealants

1. Attempted Preparation of $ClSi(OSi)_3CH_2CH_2(CF_2)_6(SiO)_3SiCl$

An attempt was made to prepare the title compound based on FCS-610 dichloride and (3,3,3-trifluoropropyl)methylcyclotrisiloxane. The title compound appears to have formed in the reaction pot according to gas chromatographic analysis. However, distillation of the reaction mixture gave a multicomponent high boiling mixture, and no pure product was obtained.

2. Preparation of FCS-610/Siloxane Copolymer Sealant

About 388 g. (0.55 mole) of FCS-610 dichloride was hydrolyzed using sodium bicarbonate-ether system. The hydrolyzate was mixed with 106 g. (0.55 mole) of $CF_3CH_2CH_2(CH_3)SiCl_2$ and 8.6 g. (0.074 mole) of $CH_2=CH(CH_3)_2SiCl$, and the mixture was stirred at 100°C for ca. 8 hrs. under a steam of dry nitrogen. The reaction mixture was dissolved in one pound of ether and treated with aqueous sodium bicarbonate solution. The ether solution was dried over Drierite and ether was evaporated *in vacuo* to yield a prepolymer. The resulting prepolymer was condensed in the presence of ca. 20 drops of tetramethylguanidinetrifluoroacetic acid solution by heating at 100°C with stirring under a high vacuum for 6 hrs. The resulting polymer was dissolved in ether, washed with dilute hydrochloric acid and aqueous sodium bicarbonate solution, and dried over Drierite. After removal of ether *in vacuo*, the viscous fluid polymer was stripped under 0.25 mm. Hg pressure at 150°C for 5 hrs. to yield 325 g. of viscous fluid polymer having a molecular weight of 17,600 (gpc). The elemental analysis and spectral data suggest that the polymer is a vinyl end blocked 1:1 molar copolymer of FCS-610 and (3,3,3-trifluoropropyl)methylsiloxane.

The polymer was found to cure by a RTV method to yield a high consistency rubber. The Tg was found to be -43°C and -39°C (by D.S.C.) for uncured and cured samples, respectively. Therefore, a significant improvement of Tg was indeed realized with this copolymer sealant. The evaluation of thermal stability of this copolymer is in progress by our TS&D group.

An additional quantity of the sealant consistency copolymer was similarly prepared and formulated. About one pound of the formulated sealant was submitted to AFML for evaluation.

3. Preparation of $Cl(CF_3CH_2CH_2)(CH_3)SiO(CF_3CH_2CH_2)(CH_3)Si(CH_2)_2(CF_2)_6(CH_2)_2Si(CH_3)(CH_2CH_2CF_3)OSi(CH_3)(CH_2CH_2CF_3)Cl$

A 500 ml., three-neck flask fitted with a water cooled condenser, a constant pressure addition funnel, a thermowell connected to a heat controller and a magnetic stirrer was charged with 184 g. (0.56 mole) of $Cl(CF_3CH_2CH_2)(CH_3)SiOSi(CH_3)(CH_2CH_2CF_3)H$ and 10 drops of 0.1 M solution of H_2PtCl_6-$6H_2O$ in isopropanol and heated to 90°C. The heat was turned down and the temperature was maintained by addition of 61 g. (0.25 mole) of $CH_2=CH(CF_2)_6CH=CH_2$. After addition, the mixture was heated to 125°C and left for one week. The reaction progress was followed by glpc analysis. The product (~45 g.) was separated by distillation through a short column under high vacuum, b.p. 203°C (0.10 mm. Hg), n_D^{26} 1.3807.

Anal. calc'd. for $C_{26}H_{36}Cl_2F_{24}O_2Si_4$: C, 30.63; H, 3.53. Found: C, 30.62; H, 3.67.

4. Hydrolysis and Polymerization of $Cl[(CF_3CH_2CH_2)(CH_3)SiO(CF_3CH_2CH_2)(CH_3)Si(CH_2)_2(CF_2)_6(CH_2)_2Si(CH_3)(CH_2CH_2CF_3)OSi(CH_3)(CH_2CH_2CF_3)]Cl$

About 38 g. (0.0372 mole) of the title compound was hydrolyzed using sodium bicarbonate-ether system. To the resulting hydrolyzate was added 0.70 g. (0.0058 mole) (1:6 ratio) of $CH_2=CH(CH_3)_2SiCl$. This mixture was stirred and heated to 80°C for ~ 72 hrs. The resulting mixture was diluted with ether and washed twice with water/sodium bicarbonate solution and once with water/sodium chloride solution and dried over Drierite. After the ether was evaporated *in vacuo*, the resulting prepolymer was condensed in the presence of ~ 5 drops of tetramethylguanidine-trifluoroacetic acid solution by heating to 80°C with stirring under a high vacuum for 4 hrs. The resulting polymer was dissolved in ether, washed twice with water and once with water/sodium chloride solution and dried over Drierite. After removal of ether *in vacuo*, the viscous fluid polymer was stripped under vacuum to 150°C for 2.5 hrs.

The polymer was found to cure by a RTV method to yield a high consistency rubber. The Tg was found to be -55°C (by D.S.C.) for the uncured polymer. DP determination by H^1 nmr was 12-14.

Anal. calc'd. for polymer DP = 12: C, 32.67; H, 3.38. Found: C, 32.4; H, 3.91.

C. Preparation of Difunctional Ethers from Perchloro-1,3-butadiene

1. Preparation of $CCl_2=CClCCl=CCl(OCH_3)$

Into 2 kg. (7.7 moles) of stirred perchlorobuta-1,3-diene, 1502 g. (7.0 moles $NaOCH_3$) of a 25% (by weight) solution of $NaOCH_3$ in CH_3OH was added slowly (addition time 3.5 hrs.). After the addition was complete, the reaction mixture was maintained at 57°C for 2 hrs., and then allowed to cool. About 4 l. of water was added and this mixture was then extracted with ether. The ether layer was separated, dired over Drierite, and was evaporated in vacuo, resulting in a residue of 1853 g. of a complex mixture which was thought to contain some unreacted starting material, $CCl_2=CClCCl=CCl(OCH_3)$, $CCl_2=CClCCl=C(OCH_3)_2$, and $CHCl_2-C(OCH_3)=CCl-C(OCH_3)_3$. The $NaOCH_3$ appears to be so much more reactive toward the perchlorobutadiene than $NaOC_2H_5$ that even adding the $NaOCH_3$ solution to an excess of the olefin did not control its tendency to form multi-methyoxylated compounds.

2. Preparation of $CCl_2=CCl-CCl=CCl(OC_2H_5)$

About 2.8 l. (ca. 83.1 moles) of absolute ethanol was added slowly to a three-neck flask containing 264.5 g. (11.5 g.-atoms) of metallic sodium. After all the sodium had reacted the solution was allowed to cool to room temperature. To this stirred solution 2 kg. (7.7 moles) of perchloro-1,3-butadiene was added dropwise (addition time 1.5 hrs.). A mild exothermic reaction occurred, resulting in the reaction temperature reaching 39°C. Two hrs. after the addition had been completed the reaction mixture was heated to 70°C for 1/2 hr. After allowing the mixture to cool, about 4 l. of water was added and this mixture was then extracted with ether. The ether layer was separated and dried over Drierite. The ether was evaporated in vacuo and the residue was distilled to give 935.8 g. (59% yield) of $CCl_2=CClCCl=CCl-(OC_2H_5)$, b.p. 82°C (0.2 mm.), n_D^{25} 1.5235. The spectral properties of the product were consistent with the assigned structure.

Anal. calc'd. for $C_6H_5Cl_5O$: C, 26.65; H, 1.86; Cl, 65.57. Found: C, 26.95; H, 1.93; Cl, 66.0.

A series of large scale reactions using the procedure above yielded a total of 6425 g. (23.8 moles) of the desired product.

3. Preparation of $CCl_2=CClCCl_2\overset{O}{\overset{\|}{C}}Cl$

a. From the $CCl_2=CClCCl=CCl(OCH_3)$ Mixture

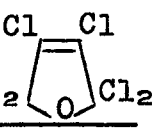
Dry chlorine was bubbled into the 1853 g. of the mixture containing $CCl_2=CClCCl=CCl(OCH_3)$ for 54 hrs. When the chlorine addition was completed, the reaction mixture was heated slowly to 130°C, allowing the rearrangement to occur. The distillation of this reaction mixture proved to be very difficult and only 318 g. (0.15 mole) of perchlorocrotonyl chloride was obtained pure.

b. From $CCl_2=CClCCl=CCl(OC_2H_5)$

Dry chlorine was bubbled into 689 g. (2.55 moles) of $Cl_2C=CClCCl=CCl(OC_2H_5)$ for 6 hrs. During the addition, an exothermic reaction heated the solution to 40°C. The reaction was monitored by glpc. When the chlorine addition was completed, the reaction mixture was heated slowly to 130°C, allowing the rearrangement to occur. The reaction mixture was distilled to yield 541.5 g. (77% yield) of the desired perchlorocrotonyl chloride, b.p. 66°C (0.6 mm.), n_D^{26} 1.5378.

Anal. calc'd. for C_4Cl_6O: C, 17.36; Cl, 76.86. Found: C, 17.6; Cl, 73.7.

The chlorination of 6.5 kg. (23.6 moles) of 1,2,3,4,4-pentachloro-1-ethoxybuta-1,3-diene was accomplished by the above method to yield 4860 g. (17.6 moles, 75% distilled yield) of pure perchlorocrotonyl chloride.

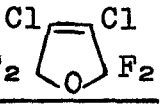
4. Preparation of 

A flask was charged with 110.5 g. (0.399 mole) of the perchlorocrotonyl chloride and 1.1 g. of $FeCl_3$. After stirring the reaction mixture at 175°C for 2.5 hrs., it was strip distilled. The distillate, 97.3 g. (88% yield), b.p. 49-64°C (0.8-2.0 mm.), crystallized upon standing at room temperature. A glpc of a CCl_4 solution of the crystals indicated them to be 99+% pure. A small amount of the crystals were recrystallized from a MeOH-H_2O solution, m.p. 37-39°C (lit.(15), 38-39°C). The

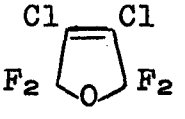
infrared spectrum was consistent with the reported spectrum of the perchloro-2,5-dihydrofuran.

Anal. calc'd. for C_4Cl_6O: C, 17.36; Cl, 76.86. Found: C, 17.50; Cl, 73.6.

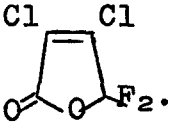
The isomerization of 4.86 kg. (17.6 moles) of perchlorocrotonyl chloride by the above method yielded 3.5 kg. (12.6 moles) of the perchloro-2,5-dihydrofuran.

5. Preparation of 

A mixture of 97.3 g. (0.352 mole) of perchloro-2,5-dihydrofuran, 125.7 g. (0.703 mole) of antimony trifluoride, and 52.6 g. (0.176 mole) of antimony pentachloride were heated to 110°C and stirred for 4 hrs. This mixture was then strip distilled at room temperature under vacuum to yield 49.5 g. (67% yield) of the desired 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran,



and 13.5 g. (18% yield) of the γ-lactone of 4-hydroxy-2,3-dichloro-4,4-difluoro-but-2-enoic acid,



A mixture of 137.7 g. (0.498 mole) of perchloro-2,5-dihydrofuran, 177.9 g. (0.995 mole) of dried antimony trifluoride, and 74.4 g. (0.249 mole) of antimony pentachloride were heated to 100°C and stirred for 2 hrs. This mixture was then strip distilled at room temperature under vacuum to yield 100.1 g. (95% yield) of the desired 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (b.p. 73-74°C). F^{19} nmr indicates a singlet at 76.5 ppm. while the infrared spectrum is consistent with the assigned structure.

Anal. calc'd. for $C_4Cl_2F_4O$: C, 22.7; Cl, 33.6; F, 36.0. Found: C, 21.7; C, 33.2; F, 37.3.

An additional 867 g. (3.13 moles) of perchloro-2,5-dihydrofuran was converted via the above method to 511 g. (2.42 moles) of the desired product and 10 g. (0.053 mole) of the lactone.

6. Preparation of $O(CF_2COOH)_2$

To a stirred mixture of 123.9 g. (0.587 mole) of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran and 617 ml. of dry acetone at room temperature, 97.5 g. (0.617 mole) of $KMnO_4$ was added incrementally over a 3 hr. period. Before strip distilling the acetone from the reaction mixture, 617 ml. of water was added to the reaction mixture. The dark brown aqueous suspension was acidified with sulfuric acid, decolorized with sulfur dioxide, and extracted with ether. The ether solution was separated, dried by filtration through magnesium sulfate, and the ether was removed in vacuo. Preliminary attempts at sublimation or recrystallization of the 83.6 g. of brown solid were unsuccessful. An infrared spectrum of the solid indicated absorption at 2,400 to 3,500 $cm.^{-1}$ (-OH), ca. 1765 $cm.^{-1}$ (C=O), 1130 to 1250 $cm.^{-1}$ (CF_2) and ca. 1090 $cm.^{-1}$ (C-O-C). These data are consistent with the solid being crude perfluorooxydiacetic acid. The crude acid was converted to the corresponding diacyl chloride without further purification.

Similarly, about 511 g. (2.42 moles) of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran was oxidized to yield 410.8 g. (82% yield) of crude perfluorooxydiacetic acid.

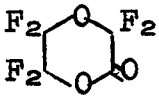
7. Preparation of $O(CF_2\overset{O}{\overset{\|}{C}}Cl)_2$

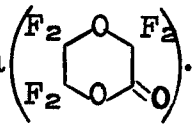
Crude perfluorooxydiacetic acid (79.4 g.) and phthaloyl chloride (200.2 g., 0.96 mole) were combined and refluxed for 6 hrs. The reaction mixture was distilled in vacuo to yield 54.0 g. of perfluorooxydiacetyl chloride, b.p. 47°C (128-144 mm.); n_D^{25} 1.3539; infrared 1800 $cm.^{-1}$ (C=O); F^{19} nmr singlet at 77.0 ppm., CF_2 (CCl_3F reference).

Anal. calc'd. for $C_4Cl_2F_4O_3$: C, 19.77; Cl, 29.19; F, 31.28. Found: C, 19.35; Cl, 28.6; F, 31.1.

8. Preparation of $O(CF_2\overset{O}{\overset{\|}{C}}F)_2$

About 20 g. (0.082 mole) of $O(CF_2\overset{O}{\overset{\|}{C}}Cl)_2$ was added in about 15 minutes to 13.5 g. (0.33 mole) of dry NaF in 165 ml. of acetonitrile. After stirring for 40 minutes at ambient temperature the reaction mixture was analyzed by glc., mass spec. and shown to be a mixture of

$O(CF_2\overset{O}{\overset{\|}{C}}F)_2$, and  . Isolation of the desired product

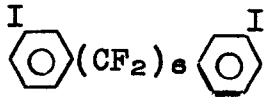
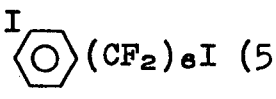
was not realized since the isomers tend to codistill. The infrared spectrum of one distillation cut (97% pure by glc) indicates absorptions at both 5.28 μ [O(CF$_2$CF)$_2$] and 5.36 μ  . Separation will be accomplished by distillation when larger samples of the material are available.

D. Coupling of I(CF$_2$)$_x$I with Aromatic Halides

1. Telomerization of CF$_2$=CF$_2$ in the Presence of ICF$_2$CF$_2$I

A 1.4 l. autoclave was charged with ICF$_2$CF$_2$I (354 g., 1.0 mole) and pressurized to 125 psi. with CF$_2$=CF$_2$. The mixture was heated to 210-250°C, cooled and the process repeated for seven cycles. Analysis of the products by glpc showed I(CF$_2$)$_2$I (4%), I(CF$_2$)$_4$I (15%), I(CF$_2$)$_6$I (24%), I(CF$_2$)$_8$I (27%), I(CF$_2$)$_{10}$I (19%), I(CF$_2$)$_{12}$I (8%), I(CF$_2$)$_{14}$I (2%) and I(CF$_2$)$_{16}$I (1%). Distillation of the mixture gave pure I(CF$_2$)$_6$I.

2. Coupling Reactions Between I(CF$_2$)$_6$I and Aromatic Halides

A flask fitted with a reflux condenser, thermometer, stirrer and N_2 purge was dried, and charged with reactants as shown in Table II. Dimethylformamide was distilled from P_2O_5 and stored over 5Å molecular seives. Powdered copper was activated with a 2% solution of I_2 in acetone. The reaction conditions are summarized in Table II, and the reaction was followed by glpc. The products from runs 1-5 were mixed with benzene and 10% aqueous HCl, filtered and the benzene layer devolatilized and analyzed by glpc. The products from run 6 were diluted with ether (200 ml.), and a solid (71.0 g.) was removed by filtration. Copper iodide (20.6 g.) was precipitated from the ether layer with water (250 ml.). The aqueous phase was extracted with ether (50 ml.) and the combined ether phases devolatilized to yield a solid (174 g.). Analysis by glpc showed unreacted m-diiodobenzene and unresolved by-products. Pure m-diiodobenzene (85 g.) was recovered by recrystallization from ethanol. The mother liquor was devolatilized to yield 17.1 g. of a residue which contained  (11 area %),  (5 area %) and

a mixture of m-diiodobenzene and unresolved by-products (8.4 area %).

E. Miscellaneous Reactions

1. Reaction of XCF_2CF_2X (X = Br, I) with $CF_3\overset{O}{\overset{\|}{C}}CF_3$/ $CF_2=CF_2$

a. $BrCF_2CF_2Br$

A solution of 117 g. (0.45 mole) of $BrCF_2CF_2Br$ and 2 g. of di-t-butyl peroxide was placed in an evacuated 300 ml. stainless steel autoclave. The autoclave was cooled to ca. -50°C and charged with 75 g. (0.45 mole) of CF_3COCF_3 and then with $CF_2=CF_2$ to a pressure of 100 psi. The reaction was heated at 125°C while rocking end-to-end. The reaction was stopped at the end of 24 hrs., during which period the pressure dropped from ca. 420 psi. (125°C) to ca. 360 psi. (125°C). Gas chromatographic analysis of the crude reaction product (145 g.) indicated the presence of three products ("a" = 39%, "b" = 18%, and "c" = 43%) in addition to $BrCF_2CF_2Br$. After removal of $BrCF_2CF_2Br$, the resulting residue was distilled to yield ca. 4 g. of pure "a", b.p. 77°C/38 mm., n_D^{26} 1.3375. The products "b" and "c" could not be isolated because of the small quantity.

On the basis of infrared, b.p. and refractive index, the product "a" is assigned $CF_3\overset{CF_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}CH_2\overset{O}{\overset{\|}{C}}CH_3$ which is formed by

Aldol condensation between acetone (from decomposition of di-t-butyl peroxide) and perfluoroacetone.

b. ICF_2CF_2I

A mixture of 71 g. (0.2 mole) of ICF_2CF_2I, 30 g. (0.3 mole) of $CF_2=CF_2$, and 66 g. (0.4 mole) of CF_3COCF_3 was placed in an evacuated stainless steel autoclave (300 ml.). The reaction was heated at 190°C for 48 hrs. while rocking end-to-end. During the reaction, pressure dropped from 850 psi. to 740 psi. (at 190°C). The reaction product was composed of 50 g. of liquid and a significant amount of solid iodine. Distillation of the liquid product gave unreacted ICF_2CF_2I and 12 g. of $I(CF_2)_4I$, b.p. 55-56°/25 mm., n_D^{26} 1.4270. The infrared absorption spectrum was identical to that of known $I(CF_2)_4I$, and the F^{19} nmr spectrum was comprised of signals

centered at δ +58.5 ppm. and δ 112.5 ppm. (reference to CCl_3F) with an area ratio of 1:1.

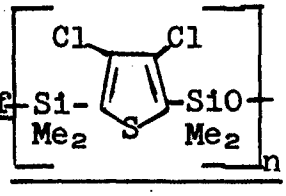
c. $BrCF_2CF_2I$

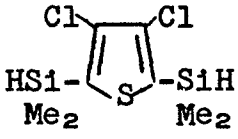
Following the procedure outlined above in (1) and (2) the reaction of $BrCF_2CF_2I$ with $CF_3COCF_3/CF_2=CF_2$ gave a very low conversion to several unidentified products.

2. Attempted Pyrolysis of Perfluoroethers

A reactor tube made of 3/4 in. nickel pipe, and packed with about 170 g. of 1/4 in. carborundum spheres, was placed in a 30 cm. long furnace. Two addition funnels, one charged with approximately 30 g. of perfluoroether, the other with approximately 150 g. of bromine, were connected to the top of the reactor tube while a water scrubber was connected to the bottom. The reactor was heated to the desired temperature (450-600°C) and purged with nitrogen. The perfluoroether and bromine were then metered in a ratio of 1:5 respectively into the heated tube over a period of 5 to 8.5 hrs.

After complete addition, the reactor was cooled and the water scrubber emptied. The resulting material was extracted with Freon® 113. The organic layer was dried and filtered. The Freon® 113 was removed in vacuo leaving an oily residue. Glpc, infrared and F^{19} nmr of the residue were taken. Reaction conditions and data derived from F^{19} nmr are recorded in Table I.

3. Preparation of 

A solution of 16 g. (0.06 mole) of 

in 50 ml. of ether was added slowly to a stirred mixture of 25 ml. of water, 25 ml. of ether, and several pieces of 0.2% Pd on carbon, at ambient temperature (ca. 20°C). The reaction mixture was stirred overnight at room temperature and filtered. The ether layer was separated and dried over Drierite. After removal of ether in vacuo, the solid hydrolyzate (no ≡SiH by infrared) was mixed with ca. 3 drops of $CH_2=CH(CF_3CH_2CH_2)SiCl_2$ and heated at 100°C for 3 hrs. while stirring under a stream of nitrogen. The resulting prepolymer was dissolved in ether, and the ether solution was washed with aqueous sodium bicarbonate and

dried over Drierite. The ether was removed *in vacuo* and the residue was stirred at 100°C *in vacuo* for 15 hrs. with four drops of tetramethylguanidine-trifluoroacetic acid solution. After cooling a stiff gummy polymer was collected.

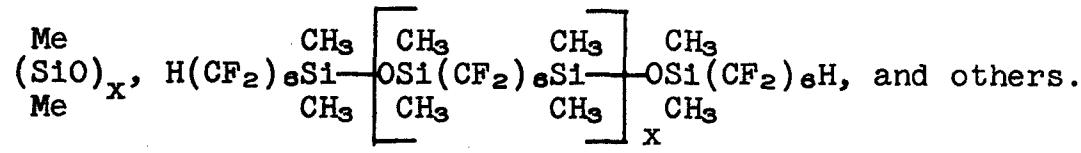
Anal. calc'd. for $C_8H_{12}Cl_2Si_2S$: C, 35.94; H, 4.53; Cl, 26.52; S, 11.99. Found: C, 34.0; H, 4.47; Cl, 23.2; S, 9.05.

The Tg of the polymer was found to be +3°C (by D.S.C.). Differential thermal analysis (10°C/min.) indicated that an oxidation began at 260°C and a rapid oxidation occurred at 480°C. Isothermal gravimetric analysis indicated ca. 14% weight loss at 250°C/24 hrs. in air and ca. 56% weight loss at 316°C/24 hrs. in air. The polymer was found to possess some fire-retardant properties and was given to AFML.

4. Hydrolysis and Attempted Polymerization of $H(CH_3)_2Si(CF_2)_6Si(CH_3)_2H$

Into a stirred slurry of 25 ml. of water, several pieces of 0.2% Pd on carbon and 25 ml. of ether was added slowly 15 g. (0.038 mole) of $HSi(CH_3)_2(CF_2)_6$-$(CH_3)_2SiH$ in 50 ml. of ether at room temperature under an atmosphere of nitrogen. After the addition, the reaction mixture was stirred at room temperature for 48 hrs. An infrared spectrum of the reaction mixture showed a strong ≡SiH band (ca. 2100 $cm.^{-1}$) along with ≡SiOH band (ca. 3300 $cm.^{-1}$). Therefore, additional Pd on carbon (ca. 15 pieces of 4-12 mesh) was introduced and the reaction mixture was continuously stirred at room temperature for seven days. The reaction mixture was filtered and the ether layer separated. Removal of ether *in vacuo* yielded a creamy white waxy solid hydrolyzate. Infrared spectrum of the hydrolyzate showed the absence of the ≡SiH function.

The waxy solid hydrolyzate was then subjected to condensation in the presence of 4 drops of tetramethylguanidinetrifluoroacetic acid at 80°C under a high vacuum with stirring. Under the conditions of polymerization, the waxy solid hydrolyzate was melted, but no apparent viscosity increase was noticed during 15 hrs. of reaction. During the reaction, a small amount of volatiles was collected in dry ice cooled trap and found to be $H(CF_2)_6H$ (by F^{19} nmr, glc, and mass spec.). The resulting reaction product was a yellowish-brown liquid and composed of more than ten components (glc). The spectral properties of the reaction product indicate the presence of



Therefore, it is apparent that an extensive cleavage of F
-C-Si≡ bond occurs under such mild conditions of F
polymerization.

5. Attempted Reaction of $C_7F_{15}Br$ with KI

A three-neck 100 ml. flask fitted with a thermometer, stirrer, and water-cooled condenser was charged with 13.3 g. (80 mmoles) of finely powdered KI, 9.0 g. (20 mmoles) of $C_7F_{15}Br$, and 50 ml. of D.M.F. The mixture was stirred with heating to 80-85° for three days. Glc analysis of a hydrolyzed aliquot indicated little, if any, reaction. Continued heating at 110° for two days resulted in the formation of small amount of gummy material. Hydrolysis of the reaction mixture yielded only a small amount of an organic layer consisting of starting material.

6. Dehydroiodination of $ICH_2CH_2(CF_2)_2CH_2CH_2I$

A one-liter, three-neck flask equipped with a water cooled condenser, a stirring rod and paddle and a constant pressure addition funnel, was charged with 51.7 g. (0.126 mole) of $ICH_2CH_2(CF_2)_2CH_2CH_2I$ in 250 ml. absolute methanol. The system was purged with dry nitrogen and the solution was heated to a mild reflux. The addition funnel was charged with 20.5 g. (0.311 mole) of 85% KOH dissolved in 100 ml. of absolute methanol. The heating was discontinued and reflux was maintained *via* addition of the KOH solution. After reacting overnight, the mixture was added to water and extracted three times with ether. The combined ether extracts were washed three times with water, dried over Drierite, and filtered through anhydrous Mg_2SO_4. Glpc pure diene, $CH_2=CHCF_2-CF_2CH=CH_2$ was isolated by a distillation. The infrared spectrum was identical in every detail with that of the diene prepared previously.

7. Preparation of $ClSi(CH_3)(CF_3CH_2CH_2)CH_2CH_2-CF_2CF_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiCl$

About 100 g. of the FCS-210 dichloride was prepared according to the method described previously(10).

8. Addition of $HSi(CH_3)_2Cl$ to $CH_2=CHCF_2CF_2CH=CH_2$

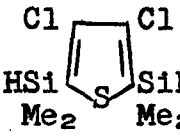
A 50 ml., three-neck flask fitted with an addition funnel, a magnetic stirrer, and a water cooled-condenser was charged with 10.8 g. (0.114 mole) of $HSiMe_2Cl$ and heated to reflux. After reflux was attained a small amount of $H_2PtCl_6 \cdot 6H_2O$ was added, the heating was discontinued, and reflux was maintained by addition of 3.9 g. (0.0253 mole) of $CH_2=CH(CF_2)_2CH=CH_2$. After the addition was completed, the reaction was maintained at reflux for 48 hrs. The reaction progress was followed by glpc. The reaction mixture has not yet been worked up.

SECTION

IV. Summary and Conclusions

The objective of this exploratory development is the synthesis and evaluation of hybrid fluorosilicone sealants for possible use as integral fuel tank sealants and other applications in high performance aircraft.

The synthesis of alpha,omega-difunctional fluorocarbon ethers was accomplished from both $BrCF_2CF_2COF$ and $FOC(CF_2)_3COF$ in which the functional groups were either bromine or iodine. An additional starting material, $FOCCF_2OCF_2COF$ was successfully prepared starting with 1,4-hexachlorobutadiene. It was found that these functional fluorocarbon ethers could be coupled to form short polymer chains using mercury. Initial studies of the coupling of alpha,omega-diiodofluorocarbons with aromatic halides were successful indicating that such compounds can be prepared in good yield.

The polymerization of the monomer,  , furnished by AFML gave a stiff gum which was given preliminary evaluation. The polymer was only moderately stable but did show some fire retardant properties. A second monomer, $HSi(CH_3)_2-(CF_2)_6(CH_3)_2SiH$, gave extensive decomposition when polymerization was attempted.

A hybrid fluorosilicone-fluoroether (FES) sealant was prepared containing the ether unit, $-CF_2CF_2O(CF_2)_{2,3}-$ in the polymer backbone. It is presently being evaluated in our laboratories.

A sample of formulated sealant (in excess of one pound) prepared as a random copolymer of FCS-610 and poly(3,3,3-trifluoropropyl)methylsiloxane was submitted to AFML (LNE) for evaluation.

Brief experimental studies were devoted to exploring the following reactions but no conclusive results were obtained and further effort is not contemplated.

1. Reaction of $CF_2=CF_2$ with $(CF_3)_2O$ in the presence of bromine or iodine and a radical initiator to form ethers.

2. The pyrolysis of commercially available fluoroethers (Fomblin®, Krytox®, and Freon® E-5) in the presence of bromine to give functional fluoroethers.

Since the original objective of the program, the achievement of reversion and fuel resistance, was met by the hybrid fluorosilicone polymer system, the course of the work has pointed toward better low temperature properties and increased oxidative resistance. Preliminary studies have shown that these objectives are feasible as discussed in the following paragraphs.

Extending the low temperature flexibility can be realized in two ways: incorporation of a fluoroether segment in place of a fluorocarbon in the polymer backbone and increasing the chain length of the siloxane portion of the backbone. Both of these routes have been amply demonstrated and will be pursued during the next contract period.

The use of segments other than $-CH_2CH_2-$ in the polymer backbone should increase oxidative stability. In particular the phenylene structure should lend itself to this use and studies are presently underway to synthesize an FCS system containing this unit.

During the ensuing contract period, it is anticipated that a large sample of a formulated FES sealant will be prepared for evaluation by AFML and Dow Corning.

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Appendix I

EXPERIMENTAL DATA

Table I

Thermal Reaction of Perfluoroethers

With Excess Bromine[a]

Run	Reactor	Packing	Rx. Temp. (°C)	N_2 (cc/min)	Ether	% Organic Material Recovered	Product Analysis CBr-F/C-F (F^{19} nmr)
1	Monel	Carborundum	450	200	Fomblin	N/A	N/A
2	Monel	Carborundum	500	200	Fomblin	N/A	0.05
3	Monel	Carborundum	550	100	Fomblin	60	0.09
4	Monel	Carborundum	600	25	Krytox	64	0
5	Monel	Carborundum	600	25	Freon E-5	74	0.07
6	Quartz	50% Alumina 50% Carborundum	500	25	Freon-E-5	2	--

(a) Continuous ether extract of aqueous layer did not give any isolable organic product.

Table II

Coupling Reaction Between $I(CF_2)_6I$ and Aromatic Halides

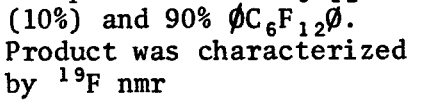
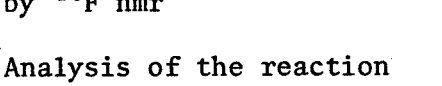
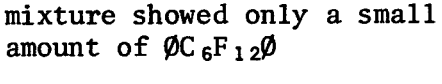
Run No.	MMoles $I(CF_2)_6I$	Mg At Cu	Ml. DMF	Aromatic Type	Aromatic MMole	Ml. C_6F_6	Temp. (°C)	Time Hrs.	Product Analysis	Remarks
1	10	79	6.0		20	0.3	110-130	18	G.l.p.c. showed $I(CF_2)_6I$ and (36%), $\emptyset C_6F_{12}I$ (30%) and $\emptyset C_6F_{12}\emptyset$ (34%)	Cu was not activated. DMF was added in stages - 2.0 ml. initially and 4.0 ml. after 15 hours.
2	10	79	2.0		20	0.3	110-130	5	G.l.p.c. showed $\emptyset C_6F_{12}I$ (10%) and 90% $\emptyset C_6F_{12}\emptyset$. Product was characterized by ^{19}F nmr	Smooth Reaction
3	10	79	2.0		20	0.3	110-140	14	Analysis of the reaction mixture showed only a small amount of $\emptyset C_6F_{12}\emptyset$	
4	20	158	15		40	7.0	110-135	43	No $\emptyset C_6F_{12}\emptyset$ was detected; however, $H(CF_2)_6H$ was isolated and identified by ^{19}F nmr	The quantity of DMF was increased significantly, however, it only increased the amount of by-product $H(CF_2)_6H$
5	20	112	15		40	0.4	130-155	13.5	Analysis of the products by G.l.p.c. and ^{19}F showed a mixture of monoalkylated products.  (22 mole %) &  (18%)	Reductive dehalogenation was significant
6	100	1000	163		500		135-150	5	Small amount of  isolated (0.5% yield)	Products of reductive dehalogenation were also found.

Table III

Preparation of $BrCF_2CF_2CF_2OCF_2CF_2Br$

Run	CsF g.	CsF Moles	$BrCF_2CF_2COF$ g.	$BrCF_2CF_2COF$ Moles	Br_2 g.	Br_2 Moles	DMF ml.	$CF_2=CF_2$ psig	$CF_2=CF_2$ hrs.	Products: Ether Free[7]	Products: Ether Containing[8]	Products: $BrCF_2CF_2CF_2OCF_2CF_2Br$	Products: $BrCF_2CF_2OCF_2CF_2Br$ + $BrCF_2CF_2CF_2OCF_2CF_2Br$
1[1]	152	1.0	228.8[4]	1.008	176	1.1	700[6]	5	16	272.8g.	--	--	--
2[2]	23	0.15	25.0[4]	0.154	26.5	0.166	80	5	16	15.6	3.6 g.	22.4 g.	--
3[3]	76	0.5	114[5]	--	100	0.625	255	15	16	125.5 g.	24 g.	--	--
4[2]	56	0.37	85[4]	0.375	75	0.47	200	13	84	67.5 g.	26.1	32.5 g.	--
5[2]	81	0.53	121.2[5]	--	122	0.76	330	15	48	96 g.	177 g.	--	--
6[2]	49.2	0.32	96[5]	--	76	0.45	320	7	16	10 g.	72 g.	--	--
7[10]										135.3[9]	--	63.5 g.	117.3 g.
												118.4	

1. Round bottom flask with stirrer
2. Agitated glass ampoule (glass ampoule in Run 4 was wrapped with aluminum foil)
3. Parr Kettle
4. Pure $BrCF_2CF_2COF$ was used.
5. Recovered $BrCF_2CF_2COF$ was used (contained CF_3CF_2Br, $BrCF_2COF$, $BrCF_2CF_2Br$ and CH_3Br according to glc/mass spec)
6. Solvent was CH_3CN
7. Distilled material containing unreacted acid fluorides and $BrCF_2CF_2Br$ but no ether.
8. Distilled material containing ethers and $BrCF_2CF_2Br$ but no acid fluorides.
9. Pure $BrCF_2CF_2Br$
10. Ether-containing material obtained from Runs 2,3,4,5 and 6 was combined and fractionated to give the product indicated.

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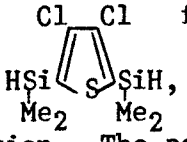
13. ABSTRACT

The objective of this exploratory development is the synthesis and evaluation of hybrid fluorosilicone sealants for possible use as integral fuel tank sealants and other applications in high performance aircraft. The synthesis of alpha,omega-difunctional fluorocarbon ethers was accomplished from both $BrCF_2CF_2COF$ and $FOC(CF_2)_3COF$ in which the functional groups were either bromine or iodine. An additional starting material, $FOCCF_2OCF_2COF$ was successfully prepared starting with 1,4-hexachlorobutadiene. It was found that these functional fluorocarbon ethers could be coupled to form short polymer chains using mercury. Initial studies of the coupling of alpha,omega-diiodofluorocarbons with aromatic halides were successful indicating that such compounds can be prepared in good yield. The polymerization of the monomer,  furnished

by AFML gave a stiff gum which was given preliminary evaluation. The polymer was only moderately stable but did show some fire retardant properties. A second monomer, $HSi(CH_3)_2(CF_2)_6(CH_3)_2SiH$, gave extensive decomposition when polymerization was attempted. A hybrid fluorosilicone-fluoroether (FES) sealant was prepared containing the ether unit, $-CF_2CF_2O(CF_2)_{2,3}-$ in the polymer backbone. It is presently being evaluated in our laboratories. A sample of formulated sealant (in excess of 1 lb.) prepared as a random copolymer of FCS-610 and poly(3,3,3-trifluoropropyl)methylsiloxane was submitted to AFML (LNE) for evaluation.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Hybrid Fluorosilicones						
Fluorocarbon-Fluorosilicones						
Fluorocarbon Ethers						
Fluorocarbon Ether Fluorosilicones						
Fuel Tank Sealants						